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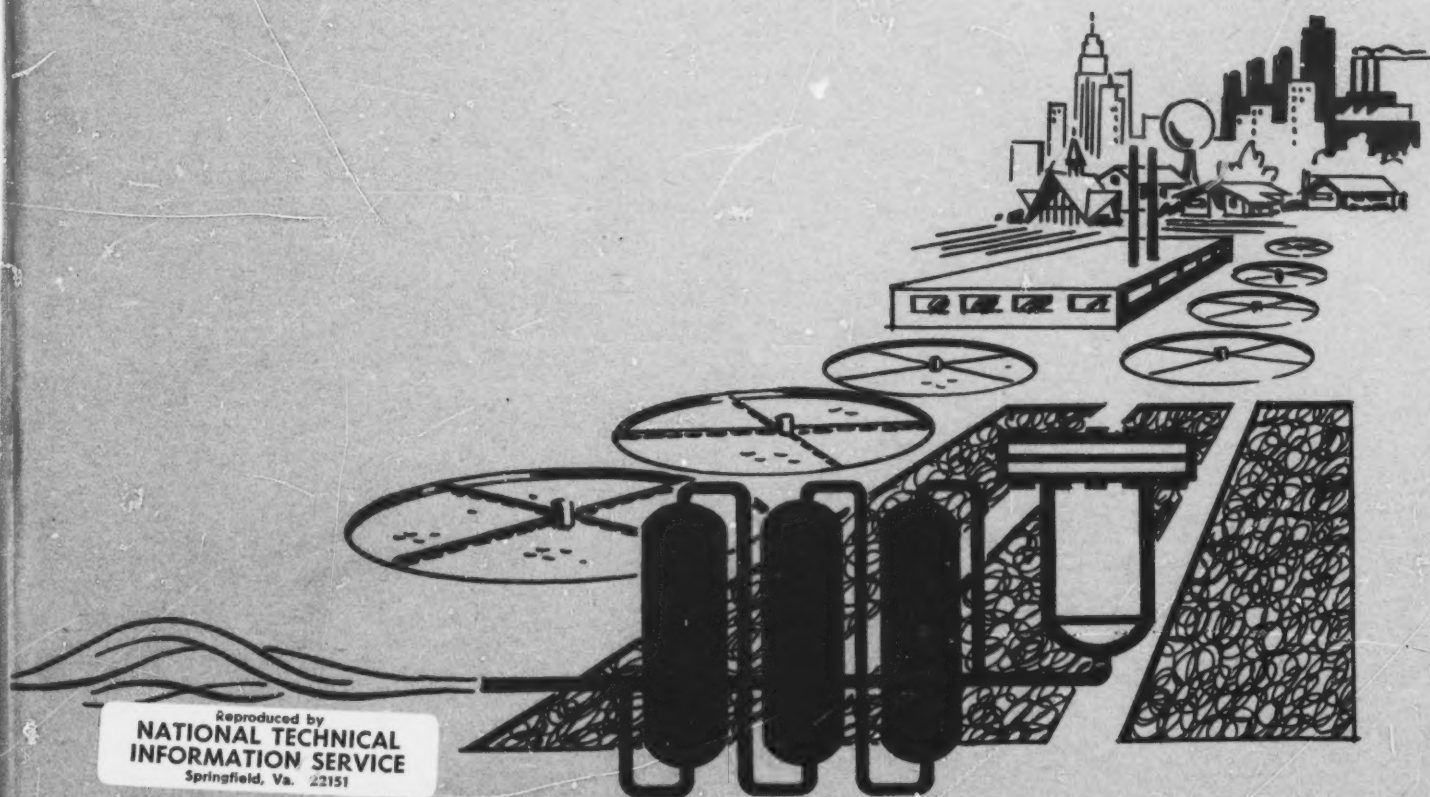
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PHOSPHORUS REMOVAL

BY

FERROUS IRON AND LIME



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16. Abstract **Spent pickle liquor, as a source of ferric ion, was added to primary treatment facilities and found to be effective in removing more than 60% of the phosphorus contained in the sewage. When advanced means for more complete removal of the insolubilized phosphates are available, removals in excess of 90% are indicated. In addition, overall suspended solids removals averaged 61.5% and BOD and COD removals averaged 61.6 and 55.3 percent during a 23 month test period. Required iron dosage ranged from the theoretical minimum of 2.7 to a maximum of approximately 3.1 weights of ferrous iron per weight of ~~ferrous iron~~ ^{phosphorus} were required. The weight increase in sludge solids due to chemical precipitation of phosphorus was 100 lbs/million gallons/mg/liter of phosphorus in the influent. Enhanced suspended solids removals represented an additional 420 lbs/mg. Total costs for treating a raw sewage containing 13 mg/l phosphorus, as typically received during this work, were estimated at \$14.17 per million gallons. (Lowry-Texas)**

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PHOSPHORUS REMOVAL BY FERROUS IRON AND LIME

by

RAND DEVELOPMENT CORPORATION

Cleveland, Ohio

and

THE COUNTY OF LAKE

Painesville, Ohio

for the

ENVIRONMENTAL PROTECTION AGENCY

Details of illustrations in
this document may be better
studied on microfiche

Project No. 11010 EGO

January, 1971

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ABSTRACT

When used in primary treatment, ferrous iron was effective in removing more than 80 percent of the phosphorus contained in sewage, with spent pickle liquor a satisfactory source of the metal ion. Required iron dosages ranged from the theoretical minimum of 2.7 to a maximum of approximately 3.1 weights of ferrous iron per weight of phosphorus contained in the sewage. When advanced means, such as filtration, are available for more complete removal of the insolubilized phosphate precipitate, phosphorus removals in excess of 90 percent are indicated.

To obtain optimum floc formation and to prevent carryover of soluble iron in the effluent the pH of the sewage had to be adjusted to the range of 7.5 to 8.0 by the addition of a strong base, such as lime. Required lime dosage was 1.6 to 1.7 weights of lime per weight of iron. Total iron in effluent was high, approximating 10 mg/l Fe, and may require filtration for removal.

Overall suspended solids removals of 61.5 percent were attained over a 23-month plant experimental program, with BOD and COD removals of 61.6 and 55.3 percent, respectively.

The supplemental use of coagulant aids was generally not beneficial.

The combined chemical cost for ferrous chloride pickle liquor and lime was \$1.09 per million gallons of sewage treated, for each mg/l of contained phosphorus. The total chemical costs for treating a sewage containing 13 mg/l of phosphorus as typically received during this work, would be \$14.17 per million gallons.

The weight increase in sludge solids due to the precipitation of phosphorus by ferrous iron and lime was approximately 100 pounds per million gallons of raw sewage per mg/l of contained phosphorus, with enhanced removals of suspended solids representing an additional 420 pounds as sludge. The sludge volume increase varied to double that obtained in normal treatment.

Filtration of the digested sludge proceeded normally and the precipitated iron phosphate remained insolubilized through anaerobic digestion. Hydraulic overloading of the digesters adversely affected digestion and subsequent settling, however, the resulting filter cake was adequately stabilized.

This report was submitted in fulfillment of Grant Project No. 11010 EGO under the sponsorship of the Environmental Protection Agency, Water Quality Office.

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Section I

CONCLUSIONS

1. The use of ferrous iron as an additive to sewage was effective in removing more than 80 percent of the phosphorus contained in the sewage.
2. Spent pickle liquor from the acid-processing of steel was a satisfactory low-cost source of ferrous iron.
3. Required iron dosage ranged from the theoretical minimum of 2.7 to a maximum of approximately 3.1 weights of ferrous iron per weight of phosphorus contained in the sewage.
4. A slight excess of iron in addition to the theoretical amount required by the phosphate demand of the sewage was necessary. The excess iron hydrolyzed to form a floc of ferrous hydroxide in which the finely-divided phosphate precipitate was entrapped and caused to settle. Otherwise, the phosphorus, although largely insolubilized as ferrous phosphate, was swept into the plant effluent.
5. It was also necessary, when ferrous iron was used in primary treatment, that the pH of the sewage as measured subsequent to the iron addition be adjusted to the range of 7.5 to 8.0 by the addition of a strong base. Unless this was done, excess soluble ferrous iron was not efficiently hydrolyzed and settled and appeared in the effluent in high concentrations. Lime was satisfactory and is the cheapest of available bases. A dosage of approximately 1.6 to 1.9 weights of lime per weight of iron was required.
6. Even with the addition of lime, total iron residuals in plant effluent were approximately 10 mg/l Fe. However, approximately 90 percent of the effluent iron was insoluble. Filtration may be required where such iron levels are not acceptable. A subsequent biological or other treatment could also reduce the effluent iron to acceptable levels.
7. A valuable by-product of the use of ferrous iron and lime for phosphorus removal in primary treatment is the enhanced removal of suspended solids and oxygen demand from the sewage. Since overall suspended solids removals were 61.5 percent and BOD and COD removals were 61.6 and 55.3 percent in an experimen-

tal operation, it may be expected that the degree of treatment will be the same or higher in future applications.

8. No additives other than the base (lime) were necessary with ferrous iron. The supplemental use of polyelectrolyte, sodium silicate and coal as further aids to sedimentation results in only incremental increases in the separation of the solids from the sewage, and did not appear to be justified by the additional cost.
9. The combined chemical cost for ferrous chloride pickle liquor and lime was \$1.09 per million gallons of sewage treated, for each mg/l of contained phosphorus. In the case of a sewage containing 13 mg/l, as at Mentor, the cost would be \$14.17 per million gallons using the unit chemical costs experienced.
10. The weight increase in sludge solids due to the precipitation of phosphates by ferrous iron and lime was approximately 100 pounds per million gallons of raw sewage per mg/l of contained phosphorus. The enhanced removals of suspended solids as sludge represented an additional 420 pounds.
11. The sludge volume increase was variable depending, in part, upon the efficiency of suspended solids removal prior to the use of iron, but in no case appeared to be double that obtained in normal treatment.
12. The operation of existing sludge digesters and dewatering facilities may be adversely affected by the additional weight and volume produced with ferrous chloride and lime additions due to overloading. However, any other procedure that has the fortunate result of increased suspended solids and phosphorus removals would similarly affect sludge digesters.
13. Precipitated phosphorus remained insolubilized through anaerobic digestion.
14. De-watering of the sludge produced from the use of ferrous iron and lime proceeded routinely, with enhanced filterability.
15. All of the mechanical requirements of the ferrous iron-lime treatment method can be met by conventional equipment properly used.

Section II

RECOMMENDATIONS

The use of ferrous iron pickle liquor and lime, as investigated in this program, is recommended as a means of removing 80 percent or more of the total influent phosphorus in a primary sewage-treatment plant. Specific recommendations include the following:

1. The pickle liquor (aqueous solution of impure ferrous chloride or sulfate) should be introduced into the sewage at the inlet end of the plant train. When adequate turbulence is not available for thorough mixing, the use of a flash-mixing step is recommended.
2. An initial iron dosage of 3.1 parts by weight of contained ferrous iron per part by weight of contained total phosphorus by weight is recommended, with subsequent empirical adjustment in each plant situation.
3. Although the rate of iron addition may be controlled manually, greater removal efficiency and economy are attained when the rate is continuously varied in proportion to the phosphorus content of the plant influent as it continually varies. The use of an automatic phosphate analyzer as a means of controlling the iron feeder is therefore recommended.
4. Hydrated lime, calcium hydroxide, is introduced subsequent to the iron addition and prior to settling. Thorough mixing is required, and the continuous preparation of the lime as a water slurry prior to mixing is recommended.
5. An initial lime dosage of 1.9 weights of hydrated lime per weight of added iron is recommended. Required lime dosage will vary according to the alkalinity of the water and the acid content of the pickle liquor, and, as in the case of iron, should be further adjusted in each situation. The introduction of only enough lime to insure a blue color in the hydroxide floc is an accurate rule of thumb for purposes of control adjustment.
6. Re-design of existing primary sedimentation units is not necessary. However, requirements for thorough mixing of the added chemicals may require the introduction of air or mechanical mixing in some locations. This would generally be true in cases where lime is added directly to the sewage in a dry form, rather than as a slurry.

If air is required, an initial rate of approximately 20.5 cubic feet per minute per MGD of sewage is recommended, with further refinements during plant operation.

7. Although the use of ferrous iron and lime results in a substantial increase in the quantity of sludge produced, it is not an inherent requirement of the method that the capacity of such equipment in existing plants be increased in every instance. Existing equipment may often be adequate, and an investigation of this possibility is strongly recommended when the cost estimate for each installation is prepared.
8. The use of ferrous iron without lime or other chemical supplements has been reported to be satisfactory for phosphorus removal in activated sludge secondary treatment, but is presently regarded with reservation for use in primary treatment ahead of trickling filters or carbon adsorption columns because of the high floc carryover from primary treatment. When lime is used with ferrous iron the effluent floc carryover is greatly reduced, suggesting that the combination might be an inexpensive and effective means of phosphorus removal in secondary plants based on processes other than activated sludge. Plant investigation of this approach is strongly recommended.
9. It is evident that any evaluation of the effect exerted by chemical additions on sewage treatment plant operation must take overall solids balances into account. However, precise data during conventional operation of the Mentor Plant are presently unavailable, except on a theoretical basis. It is therefore recommended that an empirical study of plant solids balance be undertaken to better evaluate the effect of chemical additions on the production of particulate matter throughout the treatment system.
10. Although the recommendations listed here are based on the assumption that anaerobic digestion will be used for sludge disposal, the sludge produced following sewage treatment with ferrous iron and lime may be more economically dewatered and disposed of by other methods. The investigation of methods alternative to anaerobic digestion is recommended.

Section III

INTRODUCTION

Chemical precipitation has received considerable attention as a method of separating dissolved phosphates from sewage. The addition of soluble compounds of aluminum and ferric iron has already been demonstrated to be effective; but these materials, along with the supplementary additives which are sometimes required, are relatively expensive and the investigation of cheaper additives has continued.

Ferrous iron is also reactive with soluble phosphates and is perhaps the cheapest of all potential chemical precipitants. Ferrous sulfate is produced commercially as a low cost source of iron in fertilizers. More important, ferrous iron--as either the chloride or sulfate--is also currently available at low cost as a waste by-product in the acid pickling of steel. However, the cost would increase with greater use.

This report covers an investigation of the use of ferrous iron as a phosphate precipitant in an operating primary sewage-treatment plant. The work was performed at the 4-MGD Willoughby-Mentor Wastewater Treatment Plant by the Ohio County of Lake and the Rand Development Corporation, of Cleveland, Ohio, under FWQA Grant WPRD 172-01-68.

A first objective was to determine the level of total phosphorus removal which could be attained by ferrous iron in primary treatment, and to establish by experimentation the cheapest source of ferrous iron which could be used to sustain this level. The use of supplementary additives such as lime, polyelectrolyte and ground coal, was also investigated, as were the side-effects of both the iron and the supplements.

Ferrous iron pickle liquor was found to be entirely satisfactory for the removal of more than 80 percent of the influent phosphorus, with the requirement for pH adjustment and flocculation of any excess iron met by the use of lime. Significant increases in removal of suspended solids and oxygen demand were also noted. The experimental program then continued as an investigation of the practical application of the method in an operating plant, with emphasis on matters of plant design and control, and cost.

Sections I and II of the report comprise a summary of the conclusions and recommendations. Section IV is a discussion of the Mentor Plant facility, and all facilities and resources used during the program. A brief discussion of the procedures and analyses devised to measure process efficiency, as well as detailed presentation of experimental results is included in Section V. An overall evaluation of the results is included in Section VI, in which projected costs are also listed.

Section IV

MENTOR PLANT FACILITY

The Willoughby-Mentor Wastewater Treatment Plant is located on approximately 37.6 acres of land in Mentor City, Ohio, north of Lake Shore Boulevard (S. R. 283) and approximately 1,800 feet east of Hopkins Road.

Wastewater treatment at the Mentor Plant consists of comminution, bar screening and primary sedimentation. The plant was designed for an average flow of 4,000,000 gallons per day, but hydraulic loads of up to 12,000,000 gallons per day, the design maximum, have been recorded. Throughout the body of this report the Mentor Plant is frequently referred to, since most of the experimental work pertinent to this program was carried out at that facility. Figure 1 is a layout of the plant.

This section is a summary of pertinent data concerning Mentor's influent sewage and the facilities and resources available during this program for its treatment. Mention of special conditions which influenced experimental results is made where appropriate. A brief discussion of the procedures and analyses devised to measure process efficiency, as well as the detailed evaluation of experimental results is deferred until Section V.

Description of Influent Sewage

In summary, the influent at Mentor is a high-solids wastewater with a high proportion of colloidal suspended matter. Occasional concentrations as high as 1000 mg/l total solids and 350 mg/l suspended solids have been recorded. Total phosphorus concentrations fluctuate widely throughout any given day, and typically vary between 7 and 25 mg/l, with an overall average of 13.0 mg/l as P.

Flow Rate

Flows to the Mentor Plant have increased steadily as connections to the sewerage system are completed. For example, plant reports¹ indicate the average daily flow rate has increased from 2.08 million gallons per day in 1967 to 4.36 MGD, at a design population of 40,000 persons, in 1970. In all, nearly three billion gallons of sewage were treated during the two years of this program. From June 1, 1969, the average influent flow at Mentor averaged somewhat above 3,000,000 gallons

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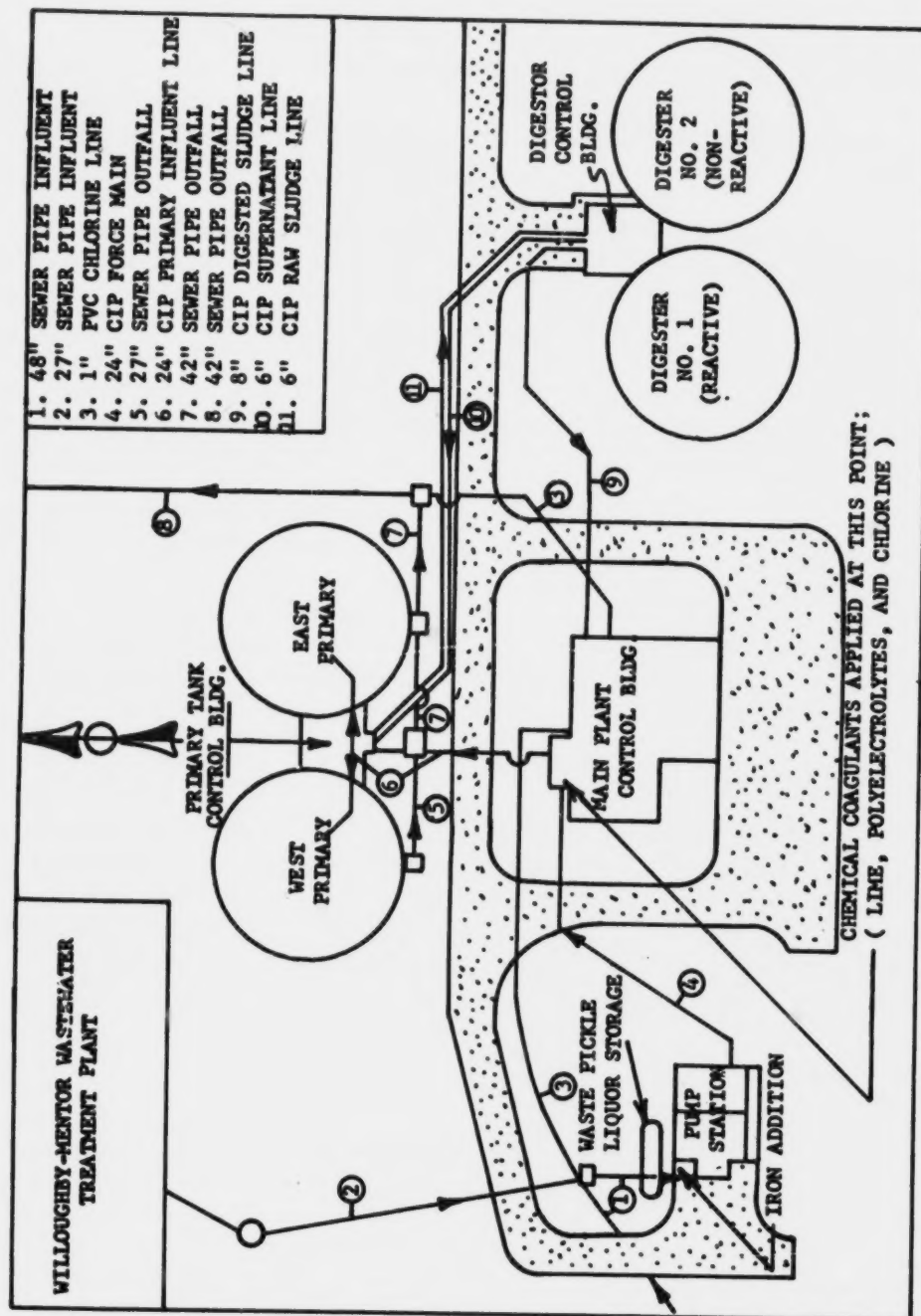


FIGURE 1
 Plan of Mentor Plant Facility

per day overall. This flow was far from uniform over a twenty-four hour period, sometimes receding to a rate of less than 1,000,000 gallons per day between 6:00 a.m. and 9:00 a.m. and gradually building to over 4,500,000 gallons per day by 1:00 p.m. The flow would then hold at this figure until approximately 6:00 p.m., thereafter decreasing slightly from 6:00 to 8:30 p.m. with a slight buildup in the late evening hours. A typical diurnal flow pattern for August 20, 1969, through August 26, 1969, is shown in Figure 2.

Solids Loading

Normally, the incoming solids are high at Mentor during the week and low on the weekends. Further variations occur when a heavy rain following a dry period flushes large quantities of solids into the plant. Hydraulic overloading accompanies such rains, reducing the overall degree of treatment that can be attained.

A specific influence on plant performance is the occasional introduction of solids on a gross basis that are not normally associated with the sewage-treatment train at Mentor. Throughout the program, primary sludge produced in the Madison, Ohio, Imhoff tanks was transported by truck to the Mentor Plant and added to the incoming raw sewage at a wet well upstream of the analytical sampling station. Adverse scheduling requirements did not permit mixing this material with Mentor's own digested sludge.

During a typical three-month period a total of 95,000 gallons of Madison sludge was thus added. Analysis of the sludge indicated an average of 10.3 percent total solids by weight (57.8 percent volatile and 42.2 percent non-volatile). Of the 82,000 pounds of solids, 90 percent were in the suspended form. There were days when as many as 4,000 gallons of sludge were added, representing 3,100 pounds of solids or 40 to 60 percent of the influent suspended solids. No deleterious effects on mechanical operation of the Mentor Plant were noted as a result of these sludge additions. Madison sludge additions were therefore regarded as a component of the sewage in this program, but the precise effects on treatment were not susceptible to separate investigation. The subject is not given further notice, but it is to be borne in mind when interpreting the influent suspended solids concentration.

There is also a large recirculating load of solids in the digester supernatant which imposes a periodic burden on the sedimentation process. The cause is traced to overloading in the sludge digesters and the re-

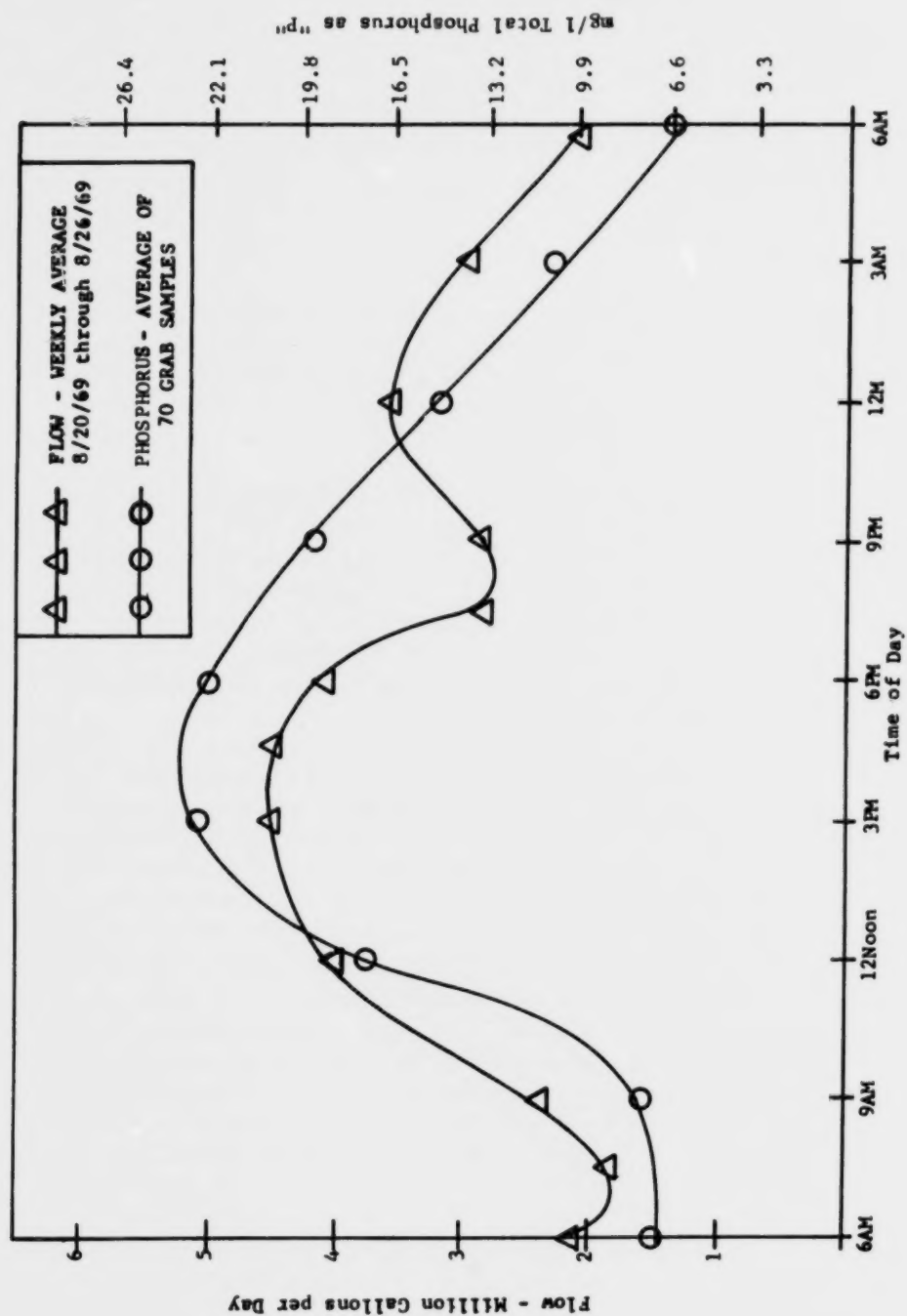


FIGURE 2
Typical Diurnal Flow and Total Phosphate Variation

sulting decreased digestion time. Approximately 0.8 percent of the plant's overall hydraulic load is digester supernatant return, but intermittent operation results in contributing nearly 35 percent of the Mentor Plant's suspended solids load during short periods. Subsequent chemical treatment with ferrous chloride and lime imposes an additional burden due to doubled sludge production.

Supernatant liquid from the digester is returned at a point where the influent flow is distributed between the two primary tanks. The precise point of return is off-center in the inlet pipe, favoring distribution to the west primary. As a result of a hydraulic imbalance, noted later is this section, most of the digester supernatant solids are subjected to extended detention times in the west primary. Study of those periods when no supernatant is added indicates that the two tanks provide unequal treatment since the west tank can operate more efficiently. The addition of supernatant solids therefore tends to equalize performance, but to an undetermined extent.

Phosphorus Concentrations

Phosphorus concentrations in the Mentor raw sewage vary widely during any single day. The total input quantity varies to an even greater degree as a result of flow variations, since the highest concentrations normally occur during the period of highest flow.

Seventy influent grab samples were averaged to investigate the fluctuations in phosphorus content over a 24-hour period. The influent samplings started at 8:00 a.m. on a Monday and showed periods of high concentration that closely paralleled the flow and which were attributed to the Monday wash day. Another 24-hour test was made on the following Thursday and results did not indicate the extreme fluctuations obtained on the previous Monday, but varied widely nonetheless. Results obtained from both of these tests indicated that phosphorus concentrations may fluctuate from 7.35 to as much as 24.70 mg/l as P, but that average concentrations of 11.60 to 15.70 mg/l during the week are more nearly typical, with an average of 13.0 mg/l overall. A typical phosphorus concentration pattern, for August 20, 1969, through August 26, 1969, is shown in Figure 2.

The proportion of orthophosphate, PO_4 , to total phosphate was also observed to vary widely and numerous tests were conducted to determine if there was a pattern to the variations. During one 48-day test in the autumn of 1968, the proportions were observed to range from 38 to 85 percent and could not be correlated with either influent total phosphorus or flow rate. The average concentration of orthophosphate

during this period was 66.4 percent of 16.6 mg/l total phosphorus as P. Since the proportion was found to be completely independent of flow rate, impracticably frequent manual monitoring would have been required to provide precise data for chemical dosing. As a consequence, all work in this program was based on total phosphorus analyses reported as "P".

Definite effluent improvement was obtained by changing the rate of ferrous chloride addition to accommodate variations in influent phosphorus concentration. It is evident in Figure 2 that the influent phosphorus concentration generally begins to increase in the late morning hours and to decline before midnight. However, more precise predictions are not feasible when based on statistical correlations. The ability to make continuous phosphorus analyses would have permitted more frequent changes in the iron feed settings and allowed feed rates to conform more closely with minimum theoretical requirements. A continuous phosphorus analyzer is therefore recommended for use in future applications.

Description of the Mentor Plant

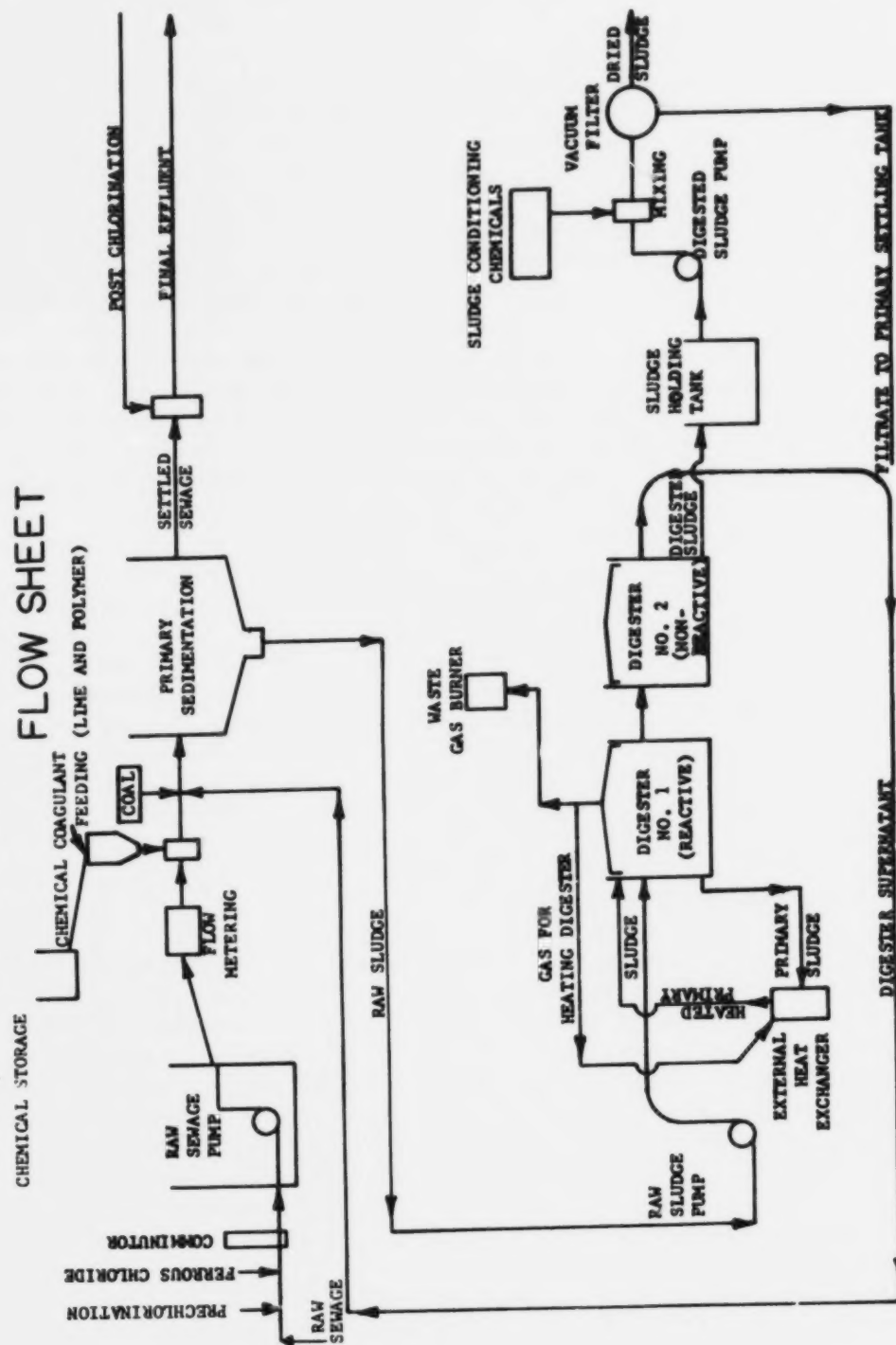
The overall plant consists of 3 main structures for plant operation: a main plant control building, primary tank control building, and a digester control building. The complete system contains a number of steps and is represented schematically in Figure 3.

The main plant control building houses the chemical feed and sludge filtering equipment, as well as a plant superintendent's office, analytical laboratory, and facilities for indoor loading of dewatered sludge. The second floor is used for chemical storage and handling to the feeders. The basement level houses equipment for pumping digested sludge from the sludge holding tank to a vacuum filter on the main floor.

The primary tank control building houses air compressors rated at 200 cubic feet per minute for primary sewage flocculation, and primary sludge withdrawal equipment on the main floor. Ventilation is provided to purge raw sludge wells prior to and during sludge drawing. The lower level houses the raw sludge pumps and associated piping.

The digester building contains the heat exchanger and required pumping and piping equipment.

FIGURE 3
WILLOUGHBY-MENTOR SEWAGE TREATMENT PLANT



Pump Station

All wastewaters enter the plant property through a 48-inch trunk sewer and a 27-inch trunk sewer and are carried to a junction manhole ahead of a pump station located on the plant property. Sewage is pumped to a 22,400-gallon wet well, providing 8 minutes detention time at an average flow of 4 MGD. Flows are manually by-passed to the outfall sewer in the event of pump station malfunction or power failure. One comminutor with an ultimate capacity of 11 MGD is provided, and provision is made for a by-pass through manually cleaned bar screens.

The pump station itself consists of four vertical non-clog pumps with motors located on an intermediate floor. Two of the units have a capacity of 2 million gallons per day and the others 4 million gallons per day. Pump operation is sequenced by a wet well liquid level control system, providing a total capacity of up to 12 million gallons per day.

Flow Metering

All influent sewage is metered by a flow tube located adjacent to the plant control building in a 24-inch cast iron force main. Facilities for by-pass of total plant flow are installed downstream from the metering device at the by-pass manhole. The plant flow is indicated, totalized, and recorded on a metering panel installed in the plant control building. The plant flow totalizer was susceptible to occasional malfunction throughout the program, requiring repairs which interrupted the experimental program and interfered with continuous data collection.

Primary Settling

Raw sewage passes from the 24-inch inlet pipe into a control chamber at the primary tank control building for distribution to the primary tanks. The wastewater discharges from the control chamber through an 18-inch cast iron pipe to the center flocculation compartment of each primary tank. Two circular primary settling tanks each 70 feet in diameter, of the combined air-flocculation and settling-compartment type, are provided. The flocculation compartments are circular, with air diffusers for mixing. Figure 4 is a view of the west primary.

The primary settling tanks provide an average detention time of 2 hours and 20 minutes at 5 million gallons per day of wastewater flow. However, changes in pumping sequence often result in variations in rates of flow of 100 GPM or more. Typical detention periods for observed



Figure 4 Overall view of the Mentor Plant from the northwest. The west primary tank is in the foreground, with the primary tank control building along-side it. The main plant control building is located at the southern end of the plant property.

flows during 1970, the last year of the program, are listed in Table I. Values are computed on the basis of the volume of the tanks between the inlet wall and the overflow weirs; flow rates are not listed for days of equipment malfunction.

Monthly average detention times, as indicated in Table I, range from 1.86 to 2.70 hours. On a daily basis the fluctuations in flow rate are even wider, ranging from 2 to 8 MGD. Actual detention time can therefore range from 1.16 to 4.66 hours over a 24-hour period. This fluctuation was observed to have a marked effect on settling efficiency during ferrous chloride and lime additions, and exerted a corresponding effect on solids removal.

Weir overflow rates are highly variable in the same approximate proportion as detention time. The extreme turbulence resulting from hydraulic overloads was observed to be the principal cause of chemical floc overflow during experimental testing. While some turbulence is

desirable for mixing purposes, the efficiency of the chemical addition procedures was affected by very high flows and minimized somewhat the degree of process optimization which could be attained.

TABLE I
Variations in Mentor Primary Plant Detention Time

Month	Avg. Rate of Flow		Detention Time In Hours
	MGD	GPM	
January, 1970	4.285	2970	2.18
February	5.008	3470	1.86
March	4.852	3360	1.92
April	4.784	3320	1.95
May	4.547	3150	2.05
June	4.587	3180	2.03
July	3.457	2400	2.70
August	3.534	2450	2.64
September	4.287	2980	2.18
October	4.046	2690	2.30
November	4.371	3040	2.13
December	4.606	3200	2.02

A more specific influence on plant performance was exerted by an imbalance in the distribution of raw sewage between the two primary tanks. The east tank carries approximately 60 percent of the hydraulic load, with a corresponding effect on detention time in each primary tank. Subsequent tables, including the performance summaries, have been weighted to give a more accurate indication of overall contaminant removals by recalculating average effluent contaminant concentrations (as mg/l) from the actual weights (in pounds) of contaminant materials handled by each primary tank.

Application of Air for Mixing Purposes

Since the influent at Mentor is divided between two primary settling tanks, the technique of introducing air into the mixing areas of one tank while eliminating air in the other was studied during iron and lime addition to determine the effect, if any, of air on flocculation efficiency. Eighty-five cubic feet of air per minute could be introduced into one tank or divided equally between both tanks. The former practice had been to operate without air since greater removals of suspended solids could be attained without its use.

Evaluations were made over two-week intervals, while the air was changed from one tank to the other at the end of each week and by dividing the air equally between the two tanks. This procedure was followed with and without chemical additions for study of the variations between the two tanks. The evaluation was hampered somewhat by the flow imbalance discussed above, but it was determined both visually and by the reductions of contaminants, that under all conditions except extreme hydraulic overloading the use of some form of mixing to enhance that obtained from normal influent turbulence was desirable. Poor mixing resulted in a cloudy supernatant high in phosphorus content. The use of approximately 20 cubic feet per minute for each MGD of sewage flow appeared optimum for the Mentor sewage. However, equipment requirements required adopting a fixed rate of 42.5 CFM, corresponding to a flow rate of 2,125,000 gallons of sewage per day, as a standard. The application of air is pictured in Figures 5 and 6.

Plant Outfall

The primary tank effluents flow over peripheral "V" notch weirs and discharge into a 48-inch diameter outfall sewer that extends into Lake Erie for a distance of approximately 2,000 feet. The design maximum of the outfall sewer is approximately 30 million gallons per day.

Chemical Feeding and Handling Equipment

A total of six different chemical additive types was of significance to the experimental program and included chlorine, coal, ferrous chloride, lime, polyelectrolyte, and sodium silicate coagulant. The following is a discussion of the equipment and procedures devised for their use.

Chlorine

Chlorination at Mentor is provided by two solution-type feeders with facilities provided for weighing, handling, and feeding from one-ton cylinders. The feeders for pre- and post-chlorination are sized to deliver chemicals at a maximum rate of 800 lbs. per day, or 24 mg/l at the design rate of flow.

Pre-chlorination facilities are currently calibrated to deliver an estimated 12 mg/l of chlorine. It can be applied at two separate points: a manhole ahead of the wet well, and a point a few feet upstream from the lime addition station, the latter case being the usual practice. Post-chlorination is applied at the effluent manhole. Chlorine is introduced to the sewage at all times for disinfection purposes; a maximum

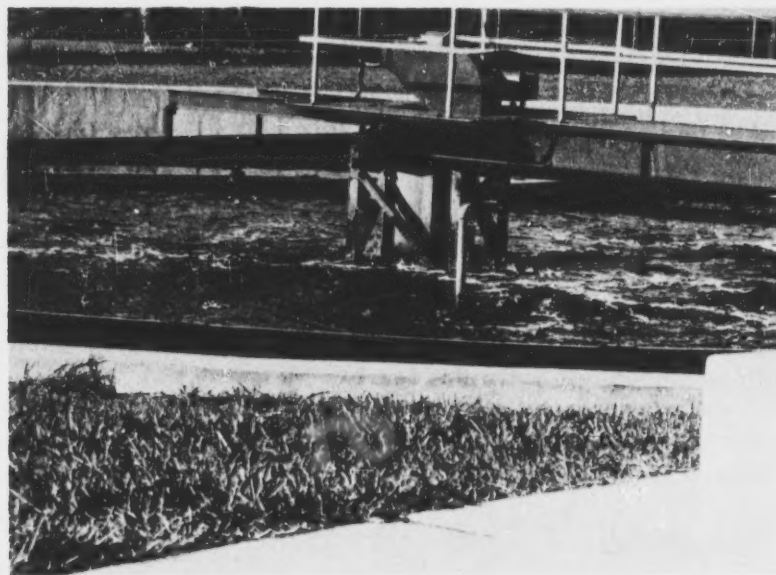


Figure 5 View of the west primary tank. Note the turbulence at the center from the applied mixing air.

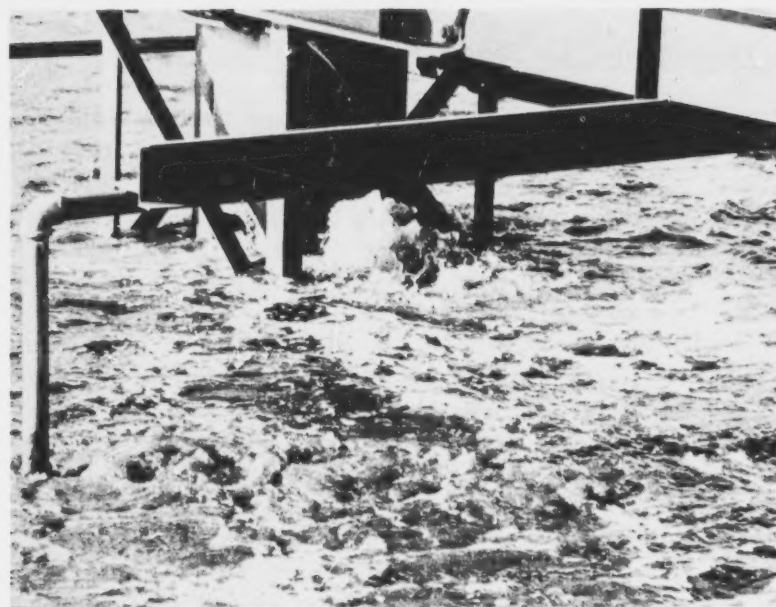


Figure 6 Enlarged view of the west primary tank. The turbulence at the center results from 42.5 CFM of air forced into the tank for mixing.

chlorine residual of approximately 4 mg/l is maintained in the plant effluent, with the outfall sewer to Lake Erie providing the necessary contact time.

During the program reported here, a study of chlorine additive levels was made to gauge the effect of such parallel additions on treatment with iron and lime, and to evaluate their effect on concentrations of residual iron and phosphorus in the effluent. None of the tests showed a noticeable effect on treatment characteristics in either case, even at concentrations in excess of 40 milligrams per liter. The subject is therefore not given further attention as a consequence, but it is to be borne in mind that under certain conditions chlorine can oxidize ferrous iron to the ferric state.

Coal Feeding

The temporary coal feeder used in this program was housed between the two primary settling tanks to facilitate delivery of the coal to either one or both of the primary clarifiers. A volumetric dry feeder of the type normally used for lime was installed.

Ferrous Chloride

The ferrous chloride pickle liquor was fed into the raw sewage upstream from the comminutor and bar screens as shown in Figures 3, 7 and 8. The basic equipment consisted of a 10,000-gallon fiberglass tank for pickle liquor storage (Figure 7), a pump for mixing the material during and after loading operations and a proportioning pump for feeding the ferrous chloride solution according to the influent flow. The quantity of iron solution added to the raw sewage influent was regulated by manual adjustment of the pump speed and percentage of pumping time.

The original iron feed pump shown in Figure 9 proved inadequate, since it was equipped with ball-check valves that became corroded by the ferrous chloride pickle liquor. The gravity-actuated valves were located on each side of the pump diaphragm and residue accumulated on the valve seats which affected the quantity of solution which could be passed. Pump motor malfunction and piping failures also contributed to the problem of maintaining a reliable feed system for the iron solution. Consistent dosing levels could not be maintained as a consequence, and steps were undertaken to revise the system.

The iron feed equipment used after March, 1970, consisted of a Moyno progressing cavity pump controlled by a variable speed drive. This

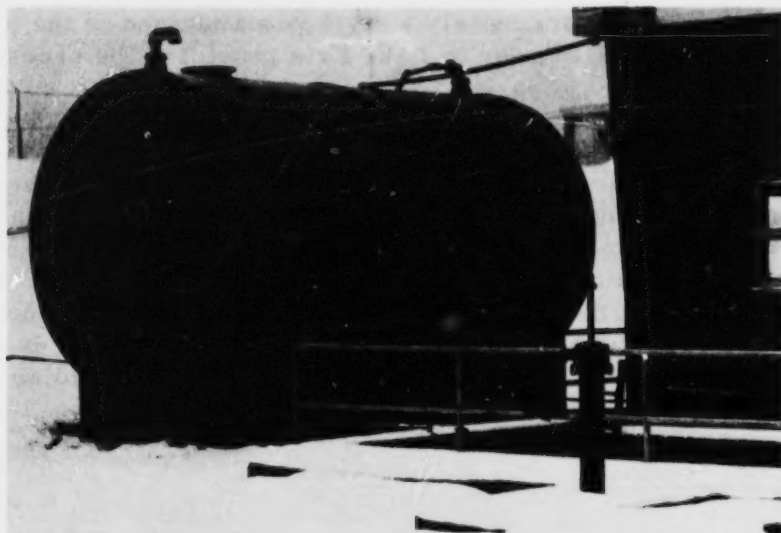


Figure 7 Waste pickle liquor reservoir. Access to the raw inlet channel is in the right foreground.



Figure 8 View from above iron delivery spigot at raw sewage inlet channel. Ferrous chloride pickle liquor was fed on a diurnal basis.

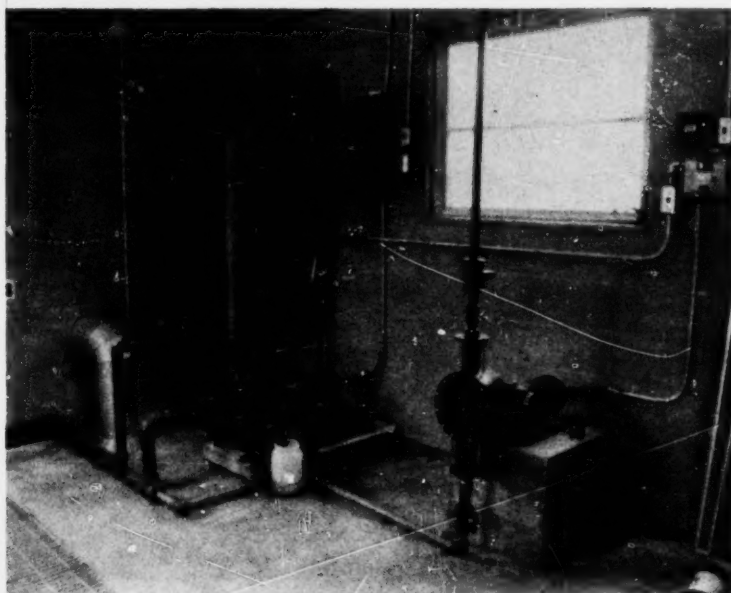


Figure 9 Original pickle liquor feed pump. The equipment was subsequently replaced by the positive displacement pump depicted in Figure 10.

pump is shown in Figures 10 and 11, and was capable of continuously supplying ferrous chloride solution from the storage tank at an average rate of approximately ten gallons per minute. A removable nylon filter was installed in the feed line between the storage tank and the pump, from which accumulated solids could be withdrawn. A coarse filter in the feed lines from the delivery truck was provided for additional protection. As with the previous chemical feed device, the pump was cycled to co-ordinate with the intermittent operation of the wet well pumps, with the cycling time dependent upon the combination of pumps necessary to keep the wet well at a constant level. The change in equipment proved adequate throughout the rest of the operation and permitted reasonably predictable feed rates to be established.

Lime

Hydrated lime in bagged form was loaded into a hopper feeding a lime batching column for wastewater coagulation (Figure 12). A collector is provided for dust control. A side stream of raw wastewater was diverted into the batching column. An adjustable solids feeder dropped the lime into the side stream where flow turbulence mixed it into the raw sewage.

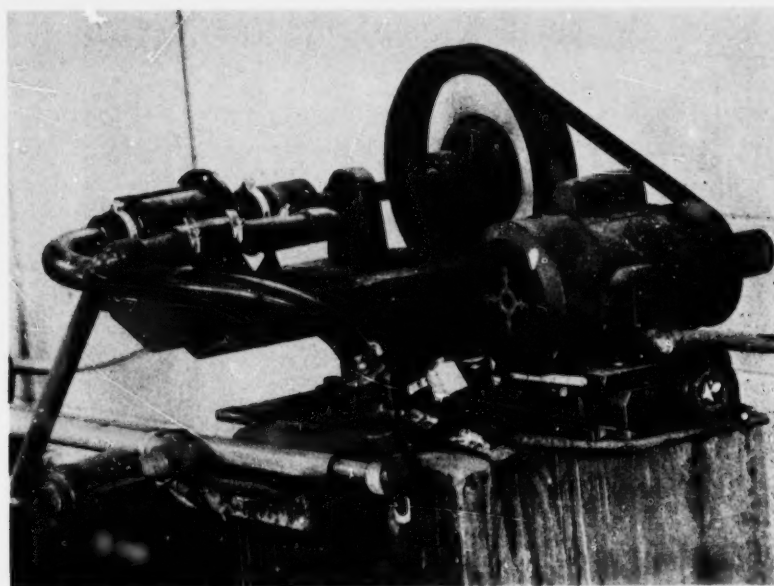


Figure 10 Positive displacement pickle liquor pump.

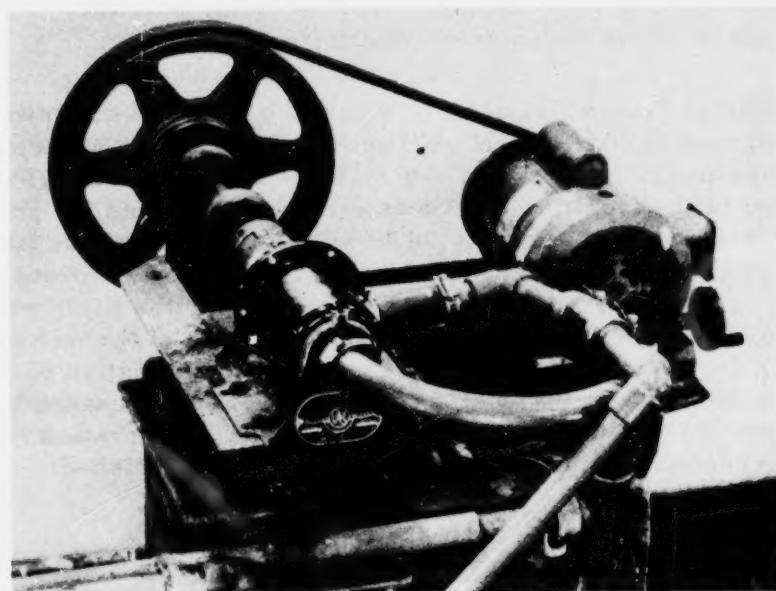


Figure 11 View of iron feed pump replacement. An alternate view of the positive displacement pump used during the latter phase of this program.

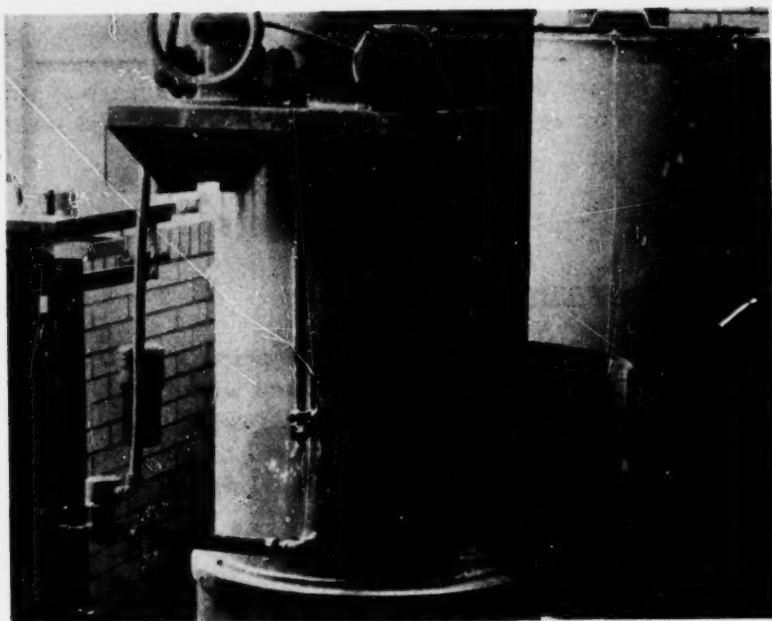


Figure 12 Lime feeder on first floor of main plant control building. Dry lime is fed to the raw sewage.

The lime feeder had been installed for other work prior to this program, and was originally intended for intermittent operation to feed lime in proportion to the volume of wastewater flow based on an electronic signal from the magnetic flow meter. The original design criteria for lime feeding equipment did not provide for feeding at the rate required in this study when the equipment was operated as a function of changes in iron feed. The dry lime feeder was therefore manually adjusted twice a day, at 12 noon and midnight. The average daily requirements could be satisfied in this manner but optimum performance could not be attained.

Polyelectrolyte

An 800-gallon polyelectrolyte solution feeder in the main plant control building was operated periodically throughout the program, with polymer metered into the raw sewage influent a few feet downstream from the lime station. Addition of polyelectrolyte was a fairly routine procedure throughout the experimental program and was suspended from time to time to examine other additive combinations.

Sodium Silicate

Additions of sodium silicate were manually charged upstream from the iron addition station by regular plant personnel and representatives of the chemical supplier.

Sludge Handling

Primary Sludge Removal

Sludge is withdrawn by gravity from each of the primary settling tanks through telescoping valves to sludge wells located with the primary tank building, and then pumped to the primary digester. The primary sludge pumps operate automatically by liquid level control equipment. Sludge may also be pumped directly from the settling tank hoppers without use of the telescoping valves or sludge wells. The scum from the primary tanks is also withdrawn into the sludge wells and pumped with the primary sludge to the digester.

Sludge Digestion and Disposal

The sludge consists of the unstabilized sediment and scum from the primary settling operation including the unseparated grit. Settled solids concentrations ranged between 4 and 7 percent. The disposal steps employed at the Mentor Plant are commonly those of digestion, filtration, and ultimate disposal by land fill.

Normal digestion is accomplished by storing the raw primary sludge for periods of up to a month or more in two 65-foot diameter tanks with a maximum sidewater depth of 18 feet 6 inches. The digesters are sometimes subjected to severe overloading with a corresponding effect on efficiency.

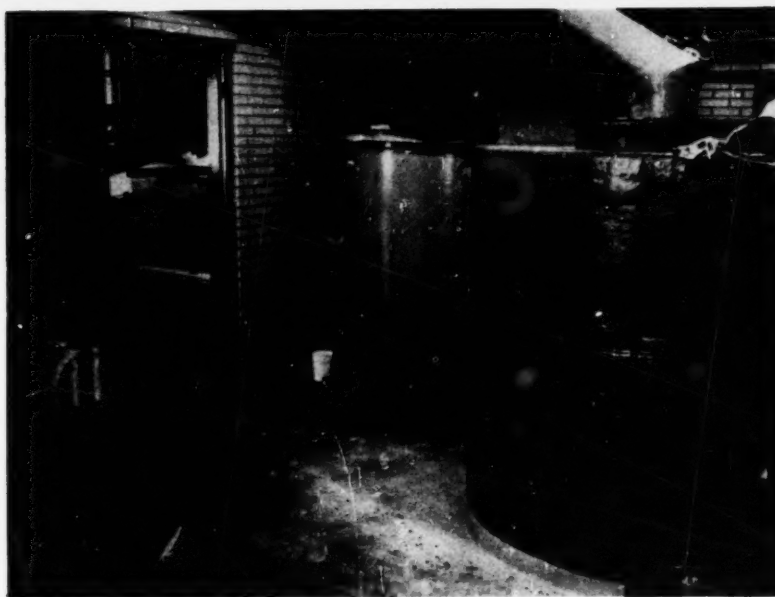
Two sludge recirculation pumps and a heat exchanger are located in the digester control building. The primary digester is reactive, with continuous mixing of the tank contents. The system was designed for the sludge to be heated to approximately 98° F. by passing it through an external heat exchanger, but overloading and cold weather conditions frequently result in temperatures ten to twenty degrees lower with occasional temperatures thirty degrees lower.

The gas produced in the digestion process is either burned at a waste gas burner or used as a fuel for the external heat exchanger. An

auxiliary natural gas supply is provided as needed to augment the gas produced in the digestion process. The sludge is then pumped to the secondary, non-reactive, digester where separation of the solids occurs by settling.

Each digester is provided with four supernatant outlets at different elevations for manual selection of supernatant draw. The supernatant from the secondary digester is returned to the raw sewage entering the primary settling tank at a point right at the stationary flow splitter. The combination of a plant hydraulic imbalance, decreased digestion time, and uneven supernatant split between the two primary tanks, results in a high suspended solids return to the west tank, as discussed earlier in this section

Digested sludge is withdrawn to a 7,500-gallon sludge holding tank at the plant control building from which it is pumped through a positive displacement pump to the sludge filtering process. In normal plant practice the sludge is first conditioned for filtration by the addition of ferric chloride solution and lime slurry stored in tanks, as pictured in Figure 13. The solids are then separated by a rotating vacuum filter, with 132 square feet of drum area.



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Figure 13 View of sludge conditioning tanks. The ferric chloride tank for sludge conditioning is in the right foreground, with the belt conveyer for filtered and dried sludge beyond the doorway. The tank to the rear of the ferric chloride reservoir is for polyelectrolyte.

Dewatered sludge from the vacuum filter is transferred by belt conveyor to dump trucks or storage vehicles for disposal, either by use as a soil conditioner or, as is most often the case, by land fill.

Section V

DATA PRESENTATION AND EVALUATION

The experimental work was performed over a period of twenty-four months and was conducted in parallel with routine plant operation. The work is divided into three categories:

1. Ferrous chloride and lime addition
2. The use of supplementary additives
3. Coal as a settling aid

Plant operations were conducted 24 hours per day seven days per week. Operating data were recorded hourly, summarized in 24-hour periods and combined with the daily analytical results. The daily summaries were then converted to monthly reports and submitted to the Ohio Department of Health.²

However, the gross data alone cannot be used for process optimization or to draw final conclusions. The ferrous chloride dosage efficiency cannot be typified by the tests using the prototype iron feed equipment for example; and to generalize on the degree of treatment without regard for plant hydraulic conditions, or the distribution of applied mixing air, could result in misleading conclusions. Also, these evaluations were done sequentially rather than simultaneously in parallel equipment. Specific operating periods are therefore selected from the gross data according to the following criteria:

1. Periods of extreme hydraulic overloading are excluded.
2. Periods of gross mechanical, electrical or supply failure are excluded.
3. When the type of additive was changed during a test the period required for attainment of equilibrium with the new additive is excluded.
4. Operating periods of less than five days are excluded when data for other tests under the same conditions are available.

The selected data are tabulated first as summaries of each type of test, twenty-five in all, with a brief description of experimental conditions which prevailed. Nine different chemical additives were evaluated, including iron, lime and coal, representing thirteen separate combinations, with the same basic equipment and procedures employed for the study of each.

1. Ferrous chloride, FeCl_2 (as pickle liquor in all cases)
2. Hydrated lime, Ca(OH)_2
3. Ferrous chloride and lime
4. Polyelectrolyte, Dow A-23

5. Ferrous chloride with Dow A-23
6. Lime with Dow A-23
7. Ferrous chloride and lime with Calgon 3000 polymer
8. Ferrous chloride and lime with Diamond 630 polymer
9. Ferrous chloride and lime with Diamond 640 polymer
10. Ferrous chloride and lime with Dow A-23
11. Ferrous chloride and lime with sodium silicate
12. Ferrous chloride and lime with coal
13. Dow A-23 with coal

Separate tables for solids removal, oxygen demand reduction, and information pertinent to phosphorus removal are given. All of the material is taken directly from the operating records and is presented in Tables XIV through XVII in the Appendix. A condensed summary of overall experimental results is included here in Table II. Further condensations of data are tabulated throughout this section as appropriate.

Analytical results are based on manually collected 24-hour composite samples, taken at the raw inlet and the primary effluent outfall for each settling tank. Grab samples were taken at several locations as required by the testing program. Routine analyses were performed in the Mentor Plant laboratory, with more specialized tests and laboratory simulations performed by specially assigned personnel. All analytical procedures were taken from "Standard Methods for the Examination of Water and Wastewater."³

It became apparent early in the experimental program that an analytical bias was introduced by the plant hydraulic imbalance discussed earlier in Section IV. Effluent analyses obtained from the two primary settlers ordinarily had been averaged to report an average value for the entire plant. However, the effect of this procedure was to unduly favor the results obtained from the west primary, which handled only 40 percent of the plant flow. Conversely the east primary was typically less efficient due to shortened detention times. The experimental results shown in Tables XIV through XVII have therefore been adjusted by recalculating average effluent concentrations from the actual weight of contaminants handled in each primary tank to equalize the effect of the hydraulic imbalance and provide a more accurate estimate of process performance.

Laboratory simulations using a jar test technique were made throughout the program to examine the mechanisms of phosphorus removal and primary sedimentation as they pertained to the use of chemical additives. Unless specified otherwise in the text, all such simulations

TABLE II
Condensed Summary of Overall Experimental Results

Test No.	Chemical Additions by Type and Combination	No. Days In Test	Raw Sewage Flow Gallons	Influent Acidity as CaCO ₃ mg/Liter	Chemical Additions mg/Liter		Suspended Solids mg/Liter	Total Phosphorus (as P) mg/Liter		pH		Effluent Iron mg/Liter	
					Fe	Other		MON	COD	IN	OUT	IN	OUT
1)	Ferrous Chloride ¹ FeCl ₂	4	10,696,000 ⁷	-	41.0	-	28.5	28.3	32.8	23.4	7.7	7.3	-
4)	Ferrous Chloride ¹ FeCl ₂	7	26,810,000 ⁸	-	49.0	-	16.0	27.0	14.7	26.0	7.5	7.0	42.5
5)	Hydrated Lime, Ca(OH) ₂	5	11,025,000 ⁷	-	-	69.6	61.0	16.7	27.4	41.8	7.4	8.5	-
6)	Hydrated Lime, Ca(OH) ₂	7	16,410,000 ⁸	-	-	63.0	53.3	17.3	34.8	44.7	7.7	8.6	-
9)	Ferrous Chloride & Lime	11	40,480,000 ⁸	-	49.0	78.0	73.8	59.2	51.7	81.6	7.3	7.6	8.7
10)	Ferrous Chloride & Lime	40	158,800,000 ⁸	-	38.8	75.0	52.0	63.2	56.3	74.8	7.6	7.6	13.2
11)	Ferrous Chloride & Lime	9	38,250,000 ⁸	48	42.2	68.7	58.8	61.9	68.4	83.2	7.5	7.7	10.8
12)	Ferrous Chloride & Lime	13	54,730,000 ⁸	26	39.6	82.0	67.9	63.2	56.2	81.4	6.9	7.9	11.0
13)	Ferrous Chloride & Lime	17	76,500,000 ⁸	21	33.7	68.3	65.2	55.7	47.8	79.8	7.4	7.2	10.6
14)	Polyelectrolyte, Dow A-23 ²	31	108,810,000 ⁹	-	-	-	0.65	28.8	32.7	0.0	7.7	7.5	-
17)	Ferrous Chloride & Dow A-23	11	50,710,000 ⁸	-	48.0	-	0.43	27.6	30.7	42.0	7.4	6.9	36.0
18)	Lime & Dow A-23	2	5,090,000 ⁸	-	-	88.0	0.47	38.0	23.1	47.4	7.3	9.1	-
19)	Ferrous Chloride, Lime & Calgon 3000	19	57,000,000 ⁸	46	47.0	101.0	0.26	70.6	51.7	85.4	7.6	8.1	8.3
20)	Ferrous Chloride, Lime & Diamond 630	11	52,272,000 ⁸	21	35.7	75.6	0.26	64.4	51.4	80.4	7.6	8.0	9.9
21)	Ferrous Chloride, Lime & Diamond 640	10	40,500,000 ⁸	21	43.0	82.0	0.25	71.4	64.0	81.5	7.2	7.5	10.4
22)	Ferrous Chloride, Lime & Dow A-23	89	397,040,000 ⁸	45	46.0	83.0	0.45	62.3	34.0	82.5	7.4	7.6	12.8
23)	Ferrous Chloride, Lime & Sodium Silicate ³	17	68,510,000 ⁸	30	46.0	87.0	13.0 ³	70.9	66.5	80.9	7.3	7.5	13.1
24)	Ferrous Chloride, Lime & Coal ⁴	22	83,600,000 ⁸	-	48.0	67.0	30.0	59.3	46.2	82.3	7.5	7.5	15.8
25)	Dow A-23 & Coal ⁵	5	15,165,000 ⁸	-	Poly ⁶ 0.74 ²	51.6	44.4	39.1	63.1	8.3	7.7	7.1	4.5

1 Pickle liquor; 7-10% Fe by weight

2 Dow A-23 polyelectrolyte; 0.3% solution

3 Grade 40 silica; 40% Na₂SiO₃

4 18 x 80 mesh coal; to east primary

5 Mius 80 mesh coal; to east primary

6 Air applied for mixing; 85.0 CFM west tank only

7 Air applied for mixing; 85.0 CFM east tank only

8 Air applied for mixing; 42.5 CFM to each tank

9 No air applied for mixing

were performed with 1000 milliliter samples in the following manner:

1. Chemical addition with rapid mixing (100 RPM) for 2 min.
2. Slow mixing (20 RPM) for 10 minutes
3. Settling for 20 minutes after mixing
4. Supernatant sampling by pipette

A variable speed stirrer (1-100 RPM range) with six shafts was used, permitting multiple sampling and comparisons.

Conclusions and comments specific to the various plant and laboratory tests are included in the text for continuity. Discussion of the process variables, with recommendations for future experimental work and for application of the recommended treatment method, are included in Section VI.

Selection of Waste Pickle Liquor as Ferrous Iron Source

Work was started in the summer of 1968 toward the design and purchase of equipment necessary to treat the Mentor influent, and an evaluation was made of alternate ferrous iron sources. Two forms of ferrous iron are most commonly available:

1. Ferrous sulfate, FeSO_4 , available in certain locations as waste pickle liquor from sulfuric acid steel pickling, but generally sold in the crystal form, copperas - $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.
2. Ferrous chloride, FeCl_2 , available mainly as waste pickle liquor, containing 7 to 10 percent iron and normally 1 to 5 percent free hydrochloric acid.

Hydrated ferrous sulfate costs approximately \$0.05 per pound of contained metal. On the basis of the minimum theoretical dosage requirements, and assuming the insolubilization of 13.0 mg/l phosphorus, as P, the minimum chemical cost would be \$14.60 per million gallons of sewage treated. Added to this would be the cost of feeding and of storage and handling equipment, since the material tends to cake in storage. If the capital costs were to be amortized over a long period, the expense is negligible. However, the costs of materials and equipment to efficiently handle large quantities of powdered ferrous sulfate on a comparatively short term basis were prohibitive.

The use of waste pickle liquor was investigated. The pickle liquor was obtained from a continuous hydrochloric acid steel-pickling operation, and was made available to the Mentor Plant simply for the cost of hauling. The cost per pound of contained iron was approximately \$0.02, or less than half that for granular ferrous sulfate, with minimum capital investment for storage.

Laboratory tests indicated that either material was suitable, the ferrous chloride form being equally effective in phosphorus insolubilization as ferrous sulfate. A contract was then let for weekly shipments at the following specifications:

Quantity	10,000 gal/week (approximate)
Iron as Fe	11.000% Maximum
Hydrochloric acid	1.000% Maximum
Manganese	0.100% Maximum
Copper	0.003% Maximum
Chromium	0.005% Maximum
Zinc	0.006% Maximum
Suspended solids	10 mg/l Maximum
Appearance	Green as opposed to brown, signifying lack of hydrolysis

A typical analysis of the material as delivered to Mentor is as follows:

Iron as Fe	10.2%
Hydrochloric acid	0.61%
Wt/gal.	10.20 pounds
Freezing point	-11°F.
Manganese	0.036%
Copper	0.001%
Chromium	0.002%
Zinc	0.002%

The iron in the material delivered to Mentor generally averaged 9.3 percent iron overall, with 0.52 percent free acid. The iron and acid ranged from 7.1 to 11.0 percent and 0.4 to 0.6 percent, respectively. The density averaged 1.20, or ten pounds per gallon.

Ferrous Chloride Precipitation; No Supplementary Additives

Bench scale studies demonstrated that thorough mixing of ferrous iron solution with raw sewage for a period of one minute or less forms an insoluble ferrous phosphate precipitate which settles only slowly over periods as long as three hours. The principal unresolved question prior to actual plant operations with ferrous chloride, then, was whether the insoluble ferrous phosphates could be induced to settle on a plant scale without the use of lime.

The ability of ferrous iron to precipitate phosphate when used alone was also demonstrated during an associated program where sewage was filtered through ground coal.⁴ When ferrous iron, as the sulfate, was added to raw sewage the average phosphorus removal was 82 per-

cent as compared to 30 percent by filtration through coal alone. A relatively low degree of pH dependence was exhibited by ferrous iron when the filter was prepared from ground coal high in pyritic sulfur. The oxidation of the pyrite released ferrous iron and acid to solution when the coal was first wetted. The highest phosphorus removals were observed during the first hours of operation when the water was acidic, diminishing rapidly with a decrease in the production of both ferrous iron and acid. The reaction of ferrous iron with soluble phosphorus was insensitive to pH at the levels tested, and near-perfect removal of phosphorus was attained whenever means were available for separation of the fine solid precipitate from the sewage stream.

Plant testing was undertaken first to provide a baseline for later evaluations. Two separate plant tests are included in Table III, characterized mainly by differing mixing air applications. The influence of air on settling is a factor in these experiments, since the work discussed in Section IV had shown 85.0 CFM to be excessive. Air was applied to a different primary during each test which permitted combining the experimental results to obtain an overall summary of performance. The analytical results listed in the combined data summary in Table III are weighted according to the proportions of flow treated in each separate test, a procedure also followed in similar tables throughout the rest of this section.

TABLE III
Overall Summary of Contaminant Removals:
Ferrous Chloride Addition Without Other Additives

Test No.	Sewage Treated Gallons	Additive mg/l Iron	Percent Contaminant Removal					Effluent	
			Suspended Solids	BOD	COD	Phos. as "P"	pH In Out	Iron mg/l	
3)	10,696,000	41.0	28.5	28.3	32.8	23.4	7.7 7.3	--	
4)	26,810,000	49.0	14.0	27.0	14.7	26.0	7.5 7.0	42.5	
Combined Results:									
	37,506,000	46.5	18.1	27.4	19.9	25.2	7.6 7.1	42.5	

In general, the addition of ferrous chloride was found to be effective in the insolubilization of phosphates on a plant scale. However, a finely-divided floc was observed to form in the settling tank, with considerable carryover into the effluent which resulted in low suspended solids removals. Treatment operations were found to be sensitive to even hourly changes in flow rate and influent sewage composition, requiring several hours to regain equilibrium.

Influent suspended solids content was variable, ranging from 136 to 316 mg/l, with an average of 193 mg/l during Test 4. Overall apparent suspended solids removals were exceptionally low throughout both of the iron-addition periods, ranging between 0.0 and 39.9 percent, respectively. Overall suspended solids removals for the combined tests was 18.1 percent which is less than removals in primary treatment without iron. Removals tended to fluctuate widely on a day-to-day basis and were observed to be mainly a function of hydraulic overloading and the accompanying weir overflow turbulence. It was evident from the turbidity and floc formation in the 24-hour composite samples that the decrease was due to carryover of finely-divided precipitates into the effluent.

Reductions in oxygen demand generally varied with suspended solids removals as would be expected in primary treatment. Overall BOD and COD removals were 27.4 and 19.9 percent respectively.

No apparent phosphorus removals higher than 42 percent were recorded in either test period. A low of zero was observed during one day of extreme hydraulic fluctuation, with a combined average of 25.2 percent attained.

At the start of iron addition the effluent was water-clear, with no visible turbidity. The two plant tests were operated consecutively and after about two days of iron addition the effluent assumed a pale yellow color with a visible, finely-divided iron floc. A portion of the dissolved iron was not hydrolyzed in the settling tank, but continued to hydrolyze in the effluent. Analyses of the effluent during Test 4 showed an average total iron concentration of 42.5 mg/l, over 80 percent of it insoluble. Careful observation indicated that the primary settlers were inefficient in collecting and removing the precipitated iron floc. It was evident that much of the light material was merely being stirred up by turbulent conditions to be discharged into the effluent.

During a parallel program at Texas City, Texas,⁵ waste ferrous sulfate pickle liquor was added directly to raw sewage prior to primary sedimentation, with insolubilized phosphate precipitates carried over

to the aeration tank of an activated sludge secondary. The secondary process provided longer detention time for reaction and more complete mixing. The precipitated phosphates and iron hydroxides were entrained in the biomass of the biological secondary and separated from the waste stream during final clarification.

However, the simple addition of iron to a primary system, without a biological secondary, necessitates the use of another chemical to increase the pH of the sewage to aid in hydrolyzing the excess iron to an insoluble floc, which can then be removed during the settling process. The most readily available chemical at Mentor which fulfilled these criteria was lime and plant testing was undertaken to define the requirements for its use.

Lime Precipitation

Table IV illustrates that the addition of lime was an effective form of treatment for phosphate removal. Treatment operations were not especially sensitive to hourly changes in flow rate and influent sewage composition. Lime treatment of raw sewage was observed to be less effective in reducing BOD than was the case with ferrous chloride addition alone or simple sedimentation. Suspended solids removals of 61.0 and 53.3 percent were also recorded which was higher than the combined 18.1 percent removal observed with ferrous chloride addition when used alone. The two separate experiments involving raw wastewater treatment with lime resulted in 41.8 and 44.7 percent removal of phosphorus, respectively, with a combined average of 43.7 percent.

TABLE IV
Overall Summary of Contaminant Removals
Lime Addition Without Other Additives

Test No.	Sewage Treated Gallons	Additive mg/l Lime	Percent Contaminant Removal					pH	
			Suspended Solids	BOD	COD	Phos. as "P"	In	Out	
5)	11,025,000	69.6	61.0	16.7	27.4	41.8	7.4	8.5	
6)	18,410,000	63.0	53.3	17.3	34.8	44.7	7.7	8.6	
Combined Results:									
	29,435,000	66.5	56.0	17.1	32.0	43.7	7.6	8.6	

Overall influent suspended solids concentrations during the two periods of lime addition were comparable to those for ferrous chloride, averaging 212 and 199 mg/l, respectively. Allowing for solids contribution by the lime itself, actual removals of influent sewage solids are presumed to be even higher than those shown in the table.

Brenner⁶ reports that calcium alone of the common mineral additives requires a high free alkalinity of the sewage to convert dissolved phosphorus to a solid form. Sufficient calcium is normally available to react with phosphorus at high pH levels, so that the lime dosage requirement is independent of phosphorus concentration. The calcium ions enter into a precipitation reaction with phosphates, approaching completion at the requisite pH of 11. Lime also reacts with the bicarbonates and with magnesium in hard water. The precipitate mixture then contains mainly calcium carbonate, calcium hydroxyapatite, and possibly magnesium hydroxide, while the effluent water is considerably softened. The resulting sludge volumes are reported to be tripled.

The addition of lime in plant tests 5 and 6 raised the pH to an overall average of 8.6, less than optimum for complete reaction, but sufficient to obtain enhanced phosphorus conversion. An examination of Table V shows that in respect to all contaminant removals, save for BOD, lime alone appeared to out-perform ferrous chloride alone for primary treatment.

TABLE V
Comparison of Contaminant Removals:
Ferrous Chloride vs. Lime Addition

Sewage Treated Gallons	Additive,		Percent Contaminant Removal					Effluent	
	mg/liter		Suspended	BOD	COD	Phos.	pH	Iron	
	Iron	Lime	Solids			as "P"	In	Cut	mg/l
37,506,000	46.5	--	18.1	27.4	19.9	25.2	7.6	7.1	42.5
29,435,000	--	66.5	56.0	17.1	32.0	43.7	7.6	8.6	--

The influence of lime on settleability also affected the apparent phosphorus removals, which increased almost two-fold with the use of lime. High removals of phosphorus had been observed with ferrous chloride addition, when taking into account the tendency of the light precipitates to carryover from the primary settlers to the effluent.

Ferrous Chloride and Lime

The use of ferrous chloride without other additives had been demonstrated to be beneficial in precipitating phosphorus, but was also found to be detrimental to settling efficiency because of the tendency of the iron-phosphate precipitate to remain in suspension. It was also evident in the tests with ferrous chloride alone that a small fraction of the dissolved iron was not hydrolyzed in the primary settlers, but continued through the sedimentation process to appear eventually in the effluent. Laboratory experiments had confirmed that the use of hydrated lime along with ferrous iron produced a more dense and particulate floc, and plant tests were therefore initiated.

The flocculation of ferrous iron is pH dependent, approaching completion only in a slightly alkaline medium. The pH of the Mentor raw sewage typically varies between 7 and 8, or near-optimum, for ideal flocculation as indicated in the laboratory. The reaction proceeds most effectively when the iron is retained in the ferrous form, denoted by a blue color in the resulting floc. The lime slurry contributed hydroxide ions which were shown in laboratory tests to promote the formation of ferrous hydroxide. The flocculation of the excess iron by lime suggested that it could be added in conjunction with ferrous chloride. Lime was therefore added to adjust the pH to a consistent level of approximately 7.5 to 8.0 and provide a medium for forming a dense floc with efficient settling properties. The average ferrous chloride dosing levels used during testing with ferrous chloride and lime varied from 43.0 to 50 mg/l as Fe. A slurry of hydrated lime, Ca(OH)_2 , was metered into the sewage downstream from the iron addition station at an average rate that varied from 55.0 mg/l in Test 7 to 103.0 mg/l in Test 8. In the absence of continuous monitoring analyses, the method of adding only enough lime to maintain the blue color was found to be an extremely sensitive means of control.

The addition of iron and lime together during preliminary tests, while demonstrably effective in reducing the phosphorus content and in improving the removal of colloidal solids from raw sewage, was of course dependent on the variable phosphorus content of the sewage. When the content of added iron exceeded that necessary to react with the contained phosphorus, virtually all of the phosphorus was precipitated, with the excess iron forming an effective floc in the presence of the lime. When the phosphorus content of the sewage exceeded the amount of available iron, most of the iron was thereby consumed in the precipitation of the phosphorus with insufficient remaining for floc formation.

The addition of lime with ferrous chloride increases the pH of the sewage to a consistent level for precipitation and is valuable in aiding the hydrolysis of the excess iron to an insoluble floc. The formation of a floc is important as a means of converting the otherwise finely-divided iron phosphates into solids of manageable size.

During the tests when iron was added on the basis of average phosphorus content it was observed that floc formation, as judged by grab samples taken from the settling tank influent, proceeded satisfactorily only in the early morning hours. Eight grab samples of raw sewage were then taken at 3-hour intervals and analyzed for phosphorus content. Results ranged between 6 mg/l at 6:00 a.m. and 38 mg/l at 3:00 p.m., confirming a deficiency of iron during the daylight hours. The iron concentrations were subsequently doubled during the daytime period of average high phosphorus content, and reduced at night. Floc formation was observed to improve noticeably, with a marked increase in the consistency of floc formation and daily phosphorus removals.

Extended plant testing was then undertaken to refine the treatment method. The results of five separate plant tests are included in Table VI, representing a total of 90 days of operation and nearly 370 million gallons of sewage treated. The application of 85 CFM of mixing air on only one primary settler in Tests 7 and 8 was shown to be excessive in earlier work and those tests are therefore omitted. As in other similar tables, the analytical results listed in the combined summaries are weighted according to the proportions of actual sewage quantities that were treated in the separate primary settling tanks.

TABLE VI
Overall Summary of Contaminant Removals:
Ferrous Chloride and Lime Addition

Test No.	Sewage Treated Gallons	Additive, mg/liter		Percent Contaminant Removal				pH		Effluent Iron mg/l
		Fe	Lime	Suspended Solids	BOD	COD	Phos. as "P"	In	Out	
9)	40,480,000	49.0	78.0	73.8	59.2	51.7	81.6	7.3	7.6	8.7
10)	158,800,000	38.8	75.2	52.0	63.2	56.3	74.8	7.6	7.6	13.2
11)	38,250,000	42.2	68.7	58.8	61.9	68.4	83.2	7.5	7.7	10.8
12)	54,730,000	39.6	82.0	67.9	63.2	56.2	81.4	6.9	7.9	11.0
13)	76,500,000	33.7	68.3	65.2	55.7	47.8	79.8	7.4	7.2	10.6
Combined Results:										
	368,760,000	39.3	74.3	61.5	61.1	55.3	78.4	7.4	7.6	11.6

The addition of ferrous chloride was found to be entirely effective for the insolubilization of phosphorus on a plant scale, with the further addition of lime effective in settling the iron-phosphate precipitate. Effluent iron concentrations were markedly reduced as a consequence. The sensitivity of ferrous chloride addition to hourly changes in flow rate and influent sewage composition was also thereby minimized.

Influent suspended solids concentrations varied during these tests in the same approximate proportions as were observed when the sewage was treated with ferrous chloride alone or lime alone, ranging from an average low of 164 mg/l in Test 9 to an average high of 193 mg/l during Test 12. Daily variations from 70 to 400 mg/l were also recorded, the latter figure attributed mainly to the addition of sludge from the Madison Plant. Overall suspended solids removal for all test periods was 61.5 percent, relatively high when hydraulic overloading and the introduction of extraneous solids to the influent is considered. Removals fluctuated less widely on a day-to-day basis than was noted during additions of ferrous chloride or lime alone. It was evident from the clarity of the effluent, even after samples were allowed to stand for several hours, that more efficient settling had occurred.

Reductions in oxygen demand were not observed to accompany increased solids removals to the extent that occurred during the lime addition periods. Overall BOD and COD removals were 61.5 and 61.1 percent, respectively, with occasional removals in excess of 75 percent observed for both contaminants.

No phosphorus removals lower than 30 percent were recorded in any test period with iron and lime, and the lower removals were attributed in every case to equipment malfunction or dosage inefficiency. Extreme hydraulic fluctuations were not as influential as even simple equipment failure. An overall combined average of 78.4 percent phosphorus removal was attained. Removals in excess of 90 percent could have been attained had means been available for removal of the iron phosphate precipitate in the effluent.

An examination of Table VII shows that in respect to all contaminant removals, the combination of ferrous chloride and lime together yielded results superior to that obtained when used separately. The value of lime additions to raw sewage treated with ferrous iron was therefore demonstrated. Contaminant removals were high, and reduced effluent iron concentrations were regarded as a valid characteristic of the method.

TABLE VII
Comparison of Contaminant Removals:
Ferrous Chloride and Lime Addition,
Separately and in Combination

Sewage Treated Gallons	Additive, mg/liter		Percent Contaminant Removal					Effluent	
	Fe	Lime	Suspended Solids	BOD	COD	Phos. as "P"	pH In	Out	Iron mg/l
37,506,000	46.5	--	18.1	27.4	19.9	25.2	7.6	7.1	42.5
29,435,000	--	66.5	56.0	17.1	32.0	43.7	7.6	8.6	--
368,760,000	39.3	74.3	61.5	61.1	55.3	78.4	7.4	7.6	11.6

Effluent Iron and Phosphorus

Iron was not regarded as a normal contaminant in this work, but was investigated in light of the possible contamination of the sewage effluent by iron in excess of that required for precipitation. There was conclusive evidence during testing with ferrous chloride alone that even when less than stoichiometric quantities of iron were used a finite residue of iron remained in the effluent.

Grab sample analysis indicated an average of 1.0 to 3.0 mg/l of iron in the plant effluent when no chemical treatment was applied. As a whole the period of ferrous chloride addition without lime was characterized by the visible formation of a hydroxide floc in the settling tanks. Analyses of the effluent showed an average iron concentration of 42.5 mg/l, ranging from 21 mg/l to 57 mg/l as an apparent function of input iron feed rates and pH fluctuations. Analysis of the plant effluent showed that over 80 percent of the iron was in an insoluble form, indicating that iron precipitation and hydrolysis reactions had been largely completed, but that maximum settling efficiency had not been attained.

Subsequent plant testing with ferrous chloride and lime together resulted in significant reductions of both total and soluble effluent iron. It can be seen in Table VII, a comparative summary of contaminant removals, that total effluent iron concentration decreased from the 42.5 mg/l recorded with ferrous chloride alone to an approximate average

of 11.6 mg/l for ferrous chloride with lime. During the tests with ferrous chloride addition alone, 80 percent of the total effluent iron was insoluble, as compared with 90 percent insoluble effluent iron during tests with ferrous chloride and lime together.

A laboratory study was undertaken to determine the ratio of soluble to insoluble forms of iron and phosphorus in the principal process streams. A standard laboratory fiberglass filter was used for solids determination. Test results indicated that over 90 percent of the effluent iron was insoluble and in suspended form and therefore amenable to separation by microstraining or filtration. Effluent phosphorus was found to be 85 percent insoluble in the same tests, and it was noted that the proportion of insoluble phosphorus compounds increased with time, eventually reaching levels in excess of 90 percent. It may therefore be presumed that retention of a chemically-treated effluent in a holding basin, or secondary process, would result in higher plant removals.

It is evident that if high concentrations of insoluble iron exist in the effluent and if the greater portion of the phosphorus in the effluent is also in an insolubilized form, then the reported phosphorus "removals" will not accurately reflect reaction efficiency. The concentrations of insolubilized effluent iron were successfully reduced, along with increased phosphorus removals, during treatment with both iron and lime as a supplement; this subject is discussed later in this report.

Since over 90 percent of the 11.6 mg/l effluent iron concentration recorded during testing with ferrous iron and lime was insoluble, it can be assumed that the actual degree of phosphorus insolubilization was higher than the 78.4 percent overall average recorded in Table VII would indicate. The theoretical weight ratio requirement of Fe:P is 2.70:1, requiring at least 7.6 mg/l of iron as Fe to insolubilize the 2.8 mg/l of effluent phosphorus noted for the combined tests. Since 10.4 mg/l of iron were available for this purpose, it is reasonable to assume that the actual degree of phosphorus precipitation was in excess of 90 percent, but not reflected in the recorded removals due to inability to permanently remove all of the precipitate from the plant stream.

Oxidation of Ferrous Iron

Numerous laboratory tests were conducted to determine the oxidation state of the iron in the chemically-treated effluent and sludge at Mentor. Since ferrous iron oxidizes rapidly to ferric at pH levels above neutral, and since ferric iron hydrolyzes under more acidic conditions than does ferrous iron⁷, it was hypothesized that the high effluent iron concentrations recorded during plant testing (42.5 mg/l) with ferrous chloride

alone could be lowered by rapid formation of ferric hydroxides above the minimum iron dosage requirements for phosphate precipitation. If so, the conditions for effective treatment (air, chemical dosage, influent chlorination) could be modified in future applications to favor oxidation.

In general, the tests showed a high degree of oxidation of ferrous iron to the ferric form. The oxygen demand of the sewage proved to be of secondary importance, since the oxidation of the iron took place before the oxygen demand of the sewage was satisfied. Laboratory findings indicated that the greater portion of iron found in both the sample sediment and supernatant was in the ferric form.

During one representative test, summarized in Tables VIII and IX, a constant weight ratio of Fe:P of 3.1:1 was maintained in a 1000 ml sample of raw sewage. Weight ratios of lime to iron were varied and the sample supernatant and sediment tested for presence of ferric iron with diphenyl phenanthroline. Molar dosage equivalents are not given to avoid mixing nomenclature as would be required in the case of lime. Samples 1, 2, 3, and 4 were prepared by adding 80, 100, 100 and 120 mg/l of lime, respectively. Tests were conducted using the laboratory procedures outlined in Section V, but with certain variations. The effect of air was determined by mixing Sample No. 4 for 30 minutes with 100 ml/min of air dispersed through a ceramic filter disc 4 square inches in area, followed by 30-minute settling. The sediment was sampled by decanting and then diluting the sample with concentrated hydrochloric acid to 100 milliliters. Aliquots were taken for analysis.

Test Conditions:	Raw Sewage	1000 ml
	Phosphorus	18.4 mg/l as P
Treatment:	Iron	60 mg/l
	Lime	varied

Test Results:

TABLE VIII
Oxidation of Ferrous Iron - Supernatant
Laboratory Test Results:

Sample No.	Weight Ratio Lime:Fe	Weight Ratio Lime:P	Sample Supernatant, mg/liter				Percent Phosphorus Removal
			Total Phos. Iron as "P"	Ferrous Iron	Ferric Iron		
1)	1.3:1	4.3:1	14.1	2.1	2.8	11.3	88.7
2)	1.7:1	5.4:1	8.8	1.5	1.9	6.9	91.7
3)	2.0:1	6.5:1	6.6	1.3	1.4	5.2	93.2
4)	2.0:1	6.5:1	4.4	2.2	1.1	3.3	88.3

TABLE IX
Oxidation of Ferrous Iron - Sediment
Laboratory Test Results:

Sample No.	Weight Ratio	Weight Ratio	Sample Sediment, mg/liter		
	Lime:Fe	Lime:P	Total Iron	Ferrous Iron	Ferric Iron
1)	1.3:1	4.3:1	42.0	8.4	33.6
2)	1.7:1	5.4:1	46.0	10.0	36.0
3)	2.0:1	6.5:1	53.0	10.9	42.1
4)	2.0:1	6.5:1	53.0	3.4	49.6

High weight ratios of ferric to ferrous iron were noted in the sample supernatants and sediments. Especially high ratios were noted when air was used for mixing.

Ferrous Chloride and Lime Dosage Requirements

The concentration of phosphorus in the raw sewage at Mentor normally varies by a factor of five or more throughout any day, with the total input quantity varying to a greater degree as a result of flow variations since the highest phosphorus concentrations normally occur during the periods of highest flow. It was therefore important that precipitants be added at a concentration sufficient to meet the phosphorus demand. Addition of an excess adds to chemical cost and increases the concentration of soluble iron in the effluent.

When ferrous chloride pickle liquor was added directly to raw sewage before primary sedimentation, without the use of supplementary additives, a negligible fraction of the phosphorus was removed in the primary process and insolubilized phosphorus precipitates were carried over into the effluent. At the theoretical weight ratio of 2.7:1, assuming ideal mixing and reaction efficiency, 100 percent phosphorus insolubilization could be attained. The actual Fe:P proportions used during test No. 3 were on the order of 3.46:1, but only 26.0 apparent percent removal was attained. However, a considerable portion of the effluent iron was present in the form of an insoluble iron-phosphate precipitate so that the degree of insolubilization could not be definitively measured simply by the extent of apparent removal.

Laboratory tests were performed to study the effect of various lime-to-iron ratios on phosphorus removal. The weight ratio of ferrous

chloride to phosphorus used was 2.3:1 as Fe to P. Lime addition ratios were then varied as a function of iron addition. Samples 1, 2, and 3 were prepared by adding 50, 75, and 100 mg/l of lime, respectively. Standard laboratory procedure was followed by an additional 20-minute settling period before analysis.

Test Conditions:	Raw Sewage	1000 ml
	Phosphorus	14.0 mg/l as P
	pH	7.9
Treatment:	Iron	45 mg/l
	Lime	varied

TABLE X

Effect of Varying Lime to Iron Ratios

Sample No.	Weight Ratio Lime:Fe	Weight Ratio Lime:P	pH	Total Soluble Phosphorus			Percent Phosphorus Removal
				Iron	Iron	mg/l concentration	
1)	1.1:1	3.6:1	8.1	8.8	1.2	3.3	76.4
2)	1.7:1	5.4:1	8.7	5.7	0.7	2.6	81.4
3)	2.2:1	7.2:1	9.1	4.3	0.6	2.1	85.0

The high lime-to-iron ratios used in this test were observed to reduce the total quantities of effluent iron and phosphorus, but exerted little effect on the ratio of insoluble to soluble iron. The increased phosphorus removals were attributed to enhanced settling and precipitation by the lime itself. The extent or relationship of these two variables could not be quantified as a general rule, however, so that dosage levels must ultimately be derived on an empirical basis in plant tests.

Table XI is a list of comparative dosage levels and removals attained with ferrous chloride and lime as indicated by the plant tests tabulated earlier. The presence in the effluent of the insolubilized iron phosphate precipitate is ignored, as is the probability of increased removals in future applications should the precipitate be permanently removed from the plant waste stream, by means such as filtration.

Inspection of Table XI shows that Tests 9 and 12 were characterized by high weight ratios in every category, yet attained phosphorus removals slightly lower than those of Test 11, in which the ratios were uniformly

the lowest. The weight ratio of iron to phosphorus used in Test 13 was lower than that required by theory for completion of the phosphorus precipitation reaction, suggesting that a finite portion of the precipitation was carried out by the lime, at a correspondingly greater chemical cost.

High lime ratios were also examined in Test 10, with phosphorus removals lower than those in Test 11 using a comparable iron to phosphorus ratio. Test 10, of 40 days duration, comprised the longest single period on the table and probably represented the most nearly typical case with no attempt at process optimization. Test 11 was a shorter period but was characterized by generally better performance in contaminant removals of all types and uniformly low chemical weight ratios that still satisfied the theoretical requirements.

TABLE XI
Overall Summary of Ferrous Iron and Lime Dosage Levels

Test No.	Additive, mg/liter		Influent Phosphorus mg/l	Weight Ratio Fe:P	Weight Ratio Lime:Fe	Weight Ratio Lime:P	Percent Phosphorus Removal
	Fe	Lime					
9)	49.0	78.0	14.1	3.4:1	1.6:1	5.5:1	81.6
10)	38.8	75.0	12.3	3.2:1	1.9:1	6.1:1	74.8
11)	42.2	68.7	13.7	3.1:1	1.6:1	5.0:1	83.2
12)	39.6	82.0	12.9	3.1:1	2.1:1	6.4:1	81.4
13)	33.7	68.3	12.9	2.6:1	2.0:1	5.3:1	79.8

Combined Results:

39.3	74.3	12.9	3.1:1	1.9:1	5.8:1	78.4
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Data from actual plant testing therefore indicate that with a 3.1:1 weight ratio of Fe:P and a weight ratio of lime to iron varying from 1.6:1 to 1.9:1, phosphorus removals of approximately 80 percent were attained. A lime to iron weight ratio of 1.9:1 is recommended for the conditions as existed at Mentor in future applications with the expectation that refinements in procedure and dosing equipment will permit reductions in the required chemical quantities. With filtration or bio-flocculation of the residual iron phosphate precipitate in the effluent, removals in excess of 90 percent may be expected.

The Use of Supplementary Additives

The addition of ferrous chloride alone was demonstrated to be beneficial in precipitating phosphorus, but was also found to be detrimental to settling efficiency because of the tendency of the iron phosphate precipitate to remain in suspension and carry over into the effluent. The use of hydrated lime produced a more dense and particulate floc and in conjunction with ferrous chloride proved to be an efficient means of separating the iron phosphate precipitate from the main plant stream. However, some iron and phosphorus, averaging 11.6 and 2.8 mg/l, respectively, remained in the effluent mainly as solids.

Tests were therefore conducted to determine the value of various supplemental additives, separately and in combination with ferrous chloride and lime. The specific purpose of these tests was to find a means of reducing effluent iron and phosphorus concentrations in a manner that would not interfere with the degree of treatment. Laboratory tests were conducted using various concentrations of ferrous iron and lime; several polymers of the anionic, cationic, and nonionic types were also tested. Order of addition, time of contact and type of mixing and flocculation were also studied. Plant tests with Dow Purifloc A-23 and Diamond Shamrock 630 and 640 polymers, and with sodium silicate are summarized in Table XII. Tests with ferrous chloride and lime, separately and in combination, are included for purposes of comparison. Laboratory results are discussed where pertinent throughout the text.

Polyelectrolyte Polymer

The principal form of chemical treatment employed by the Mentor Plant prior to the start of this program involved the use of Dow A-23 polymer as a settling aid. Three separate plant tests were conducted with this material for comparison with the results obtained with ferrous chloride and lime addition. The original tests were characterized mainly by differing air applications. The influence of air on settling was a factor in these experiments, since parallel work had shown 85.0 CFM to be excessive and detrimental to settling efficiency. Air was applied to different primary settlers during Tests 15 and 16 and these tests are therefore not included. Test 14, however, covered a 31-day operating period under stable conditions without any application of air and is considered indicative of the overall degree of treatment typically attained by the Mentor Plant. Overall results for Test 14 are listed in Table XII.

It is evident that since polymer is not itself a phosphorus precipitant the principal advantage commending its use is enhanced settling. In-

TABLE XII
Comparison of Overall Contaminant Removals:
Ferrous Chloride, Lime, and Supplementary Additives

Test ¹ No. by Type and Combination	Total No. Days	Raw Sewage Flow Gallons	Chemical Additions mg/Liter		Suspended Solids		BOD %Red	COD %Red	Total Phosphorus (as P) %Red		pH		Effluent Iron mg/Liter OUT
			Fe	Lime	Other	%Red			%Red	%Red	IN	OUT	
Ferrous Chloride, 2 FeCl ₂	11	37,506,000 ⁵	46.5	--	--	18.1	27.4	19.9	25.2	7.6	7.1	42.5	
Hydrated Lime, Ca(OH) ₂	12	29,435,000 ⁵	--	66.5	--	56.0	17.1	32.0	43.7	7.6	8.6	--	
Ferrous Chloride & Lime	90	368,760,000 ⁶	39.3	74.3	--	61.5	61.1	55.3	78.4	7.4	7.6	11.6	
14) Polyelectrolyte, Dow A-23 ³	31	108,810,000 ⁷	--	--	0.65	56.1	28.8	32.7	0.0	7.7	7.5	--	
17) Ferrous Chloride & Dow A-23	11	50,710,000 ⁶	48.0	--	0.43	5.2	27.6	30.7	42.0	7.4	6.9	36.0	
18) Lime & Dow A-23	2	5,090,000 ⁶	--	88.0	0.47	38.0	23.1	32.6	47.4	7.3	9.1	--	
19) Ferrous Chloride, Lime & Calgon 3000	19	57,000,000 ⁶	47.0	101.0	0.26	70.6	51.7	64.6	85.4	7.6	8.1	8.3	
20) Ferrous Chloride, Lime & Diamond 630	11	52,272,000 ⁶	35.7	75.6	0.26	64.4	51.4	50.3	80.4	7.6	8.0	9.9	
21) Ferrous Chloride, Lime & Diamond 640	10	40,500,000 ⁶	43.0	82.0	0.35	71.4	64.0	50.0	81.5	7.2	7.5	10.4	
22) Ferrous Chloride, Lime & Dow A-23	89	397,040,000 ⁶	46.0	83.0	0.45	62.3	34.0	61.0	82.5	7.4	7.6	12.8	
23) Ferrous Chloride, Lime & Sodium Silicate ⁴	17	68,510,000 ⁶	46.0	87.0	12.0 ⁴	70.9	66.5	52.8	80.9	7.3	7.5	13.1	

¹ Refers to results of single test listed only; all others combined results for type of chemical addition

² Pickle liquor; 7-10% Fe by weight

³ Dow A-23 polyelectrolyte; 0.3% solution

⁴ Grade 40 silicate; 40% Na₂SiO₃

⁵ Results from two different tests; 85.0 CFM air to different primary in each

⁶ Air applied for mixing; 42.5 CFM to each tank

⁷ No air applied for mixing

spection of Table XII shows that the suspended solids removal with A-23 was approximately 56 percent.

Reductions in chemical oxygen demand were generally a function of suspended solids removal. BOD removals were uniformly low for all three forms of treatment, with lime addition actually appearing to be detrimental as discussed earlier in this section. Lime dosage was however not optimized for its use as a sole additive.

It is apparent that the addition of polymer on a plant scale was more effective than separate additions of ferrous chloride or lime in every respect, save that of phosphorus removal. The fine polyelectrolyte floc was observed to spread uniformly through the primary settler and to aid in settling, with minimum effluent turbidity.

Ferrous iron or lime when used alone resulted in an effluent with high contaminant concentrations. Iron without lime resulted in an unsightly brown effluent with a suspended solids content only slightly reduced from that of the influent. Numerous laboratory tests showed that polymers were not capable of settling the insolubilized iron-phosphate precipitate to any significantly greater degree than normal primary sedimentation alone.

Reference to Table XII shows that the average removal of suspended solids during a plant test with ferrous chloride and polymer was 5.2 percent. The removals of BOD and COD were 27.6 and 30.7 percent, respectively. Phosphorus removals averaged 42.0 percent. These results do not differ greatly from those obtained from the use of ferrous chloride alone. The reduction in oxygen demand was not observed to be significantly different from that attained when polyelectrolyte alone was added. However, the contribution of solids by ferrous chloride addition apparently counterbalanced the influence exerted by polymer on settling, resulting in negligible net overall removals. Some settling of the insolubilized iron-phosphate precipitate undoubtedly occurred, but at the expense of overall performance. The use of polymer and ferrous chloride together is therefore considered to be the most unfavorable additive combination tested.

The use of 66.5 mg/l lime alone was shown in Tests 5 and 6 to yield more acceptable results than ferrous iron alone; however, the overall contaminant reductions were poor. The tabulated figures in Table XII show somewhat improved contaminant removals by the use of 0.47 mg/l polyelectrolyte in conjunction with 88.0 mg/l of lime. It was observed that the disparity in performance between the primary settling tanks was much less when polymer was used. Air was alternately

applied to each primary tank during lime addition, with a corresponding narrower spread in performance results. In any case, the data indicate that settling efficiency was diminished, with suspended solids removals declining from 56.0 percent with lime addition to 38.0 percent when polymer and lime were used together. The use of a polymer therefore did not improve the results obtained with lime addition and, in respect to solids removal, was detrimental.

The final step in the sequence of testing was to use polymer as a supplement to ferrous iron and lime additions. Numerous laboratory tests were conducted to determine if polyelectrolyte compounds could be of use in aiding the settling of the iron-phosphate precipitate and in so doing improve overall phosphorus removals and reduce effluent iron concentrations. As discussed earlier in this report, phosphorus removals in excess of 80 percent were obtained using ferrous chloride and lime.

Because settling conditions in full scale operation are more variable than in the laboratory, tests were run on settling rates using various concentrations of A-23 polyelectrolyte along with 60 mg/liter of iron and 80 mg/liter of lime. Settling rate was definitely increased by increasing amounts of polymer up to 1.25 mg/l with as little as 0.1 mg/l showing only slightly faster settling rates than tests with no polymer. The function of settling vs time appeared to be straight line with about ten minutes settling time required with no polymer. Greatest efficiency was achieved only with the high polymer concentrations.

The effect on settling of the insolubilized iron-phosphate precipitate was determined by taking grab samples of untreated raw sewage and controlling the dosage of the chemical additives. The following test was a typical example.

Test Conditions:	Raw Sewage	1000 ml
	Phosphorus	15.1 mg/l
	Acidity as CaCO_3	65 mg/l
Treatment:	55 mg/l Iron	
	75 mg/l Lime	

Test Results:

Polymer Added	Percent Phosphorus Removal
1) No polymer added	82.5
2) 0.5 mg/l Dow A-23	83.5
*3) 0.5 mg/l Dow A-23	83.0

* Polymer added 4 min. after lime addition

The results indicated that no significant change in phosphorus removal occurred as a result of polymer addition.

The polymer tested in the following experiment was "Atlasep 2A2" of the weak-moderate anionic form. Supplementary additions of iron were made to a sample of raw sewage to better gauge the effect of polymer addition.

Test Conditions:	Raw Sewage	1000 ml
Treatment:	Total Iron	120 mg/l
	Lime	130 mg/l
	Polymer	varied

Test Results:

Polymer Added	Total Iron mg/l
1) No polymer added	23.0
2) 0.1 mg/l "2A2" before lime	31.0
3) 0.5 mg/l "2A2" before lime	31.0
4) 0.1 mg/l "2A2" after lime	18.0
5) 0.2 mg/l "2A2" after lime	18.0
6) 0.5 mg/l "2A2" after lime	18.0

No significant change in residual iron content of the effluent was observed when the polymer was added after the lime; however, the addition of polymer before the lime appeared to increase the effluent iron content.

A great many polymer types--over thirty in all--were evaluated in the laboratory and found to be equally ineffective in reducing effluent phosphorus and iron. Results with the six tested in the following experiment typify the results obtained.

Test Conditions:	Raw Sewage	1000 ml
	Phosphorus	11.4 mg/l as P
Treatment:	Iron	57 mg/l as Fe
	Lime	80 mg/l
	Polymer	0.3 mg/l

Test Results:

Polymer Added	Phosphorus as "P"	Total Fe	Percent Phosphorus Removal
	mg/liter		
1) No polymer added	1.6	18.5	86.0
2) Allstate #6	1.3	15.9	88.6
3) Atlasep 2A2	1.3	14.6	88.6
4) Atlasep 5A5	1.3	12.3	88.6
5) Calgon 3000	1.6	15.0	86.0
6) Calgon WC 618	1.3	14.1	88.6
7) Nalco D 2339	1.3	14.1	88.6

No significant reductions of effluent phosphorus beyond that obtained with iron and lime alone were observed. The slightly lower removals recorded in Tests 1 and 5 were accompanied by an equally slight rise in effluent iron content.

In light of the work described above, plant testing was undertaken to acquire data for comparison with ferrous chloride and lime treatment. Four separate plant tests are included in Table XII, along with the combined summary of results obtained with ferrous chloride and lime. All data are derived from the tables introduced at the beginning of this section.

In general, the addition of polyelectrolyte was found to result in an overall degree of phosphate removal that was slightly superior to that attained with ferrous chloride and lime alone although the significance of the slight improvement is questionable. Suspended solids removals for the two tests were ten percent higher. BOD removals were notably lower for the Dow A-23 tests, averaging 34.0 percent.

An examination of the results listed in Table XII shows that Tests 19 and 21 using Calgon 3000 and Diamond 640 polymers, yielded the most favorable results. Contaminant removals were generally higher than those obtained with the other polymers.

A comparison of results in Table XII shows that the addition of lime was the most significant factor. The lime:iron ratio without polymer was 1.9:1, as compared with ratios of 2.1:1 and 2.2:1 used during supplemental additions with polymer.

The uniform addition of large amounts of lime means that little opportunity for dosage deficiency exists on an hour-to-hour basis; and while this results in increased chemical feed, enough lime is available at a given time to meet the lime demand exerted by iron addition. Increased efficiency of settling and phosphorus precipitation with increased removals, and minimization of effluent iron all follow as a consequence. The addition of ferrous chloride and lime together was sufficient to attain high levels of performance, but removals were further enhanced by supplements of polymer. Polymer may or may not prove beneficial where iron and lime dosages are optimized.

Sodium Silicate

Sodium silicate was investigated as an additive with iron and lime in both laboratory and plant tests. The silicate which was not activated before use produced no significant improvement in treatment. Results of the plant test are shown in Table II.

Settling With Coal

Ground coal sized to 18 x 80 mesh was used as an additive with iron and lime while minus 80 mesh ground coal was used with Dow A-23 polymer. Laboratory tests indicated that a small dense floc which settled faster than floc without coal was produced. Results of plant tests, however, as shown in Table II, indicate that treatment was not significantly improved by the coal.

Sludge Handling

The use of iron and lime adds to the weight and volume of sludge, most of which is due to phosphate removal and higher suspended solids removals. The remaining portion consists of calcium carbonate and iron hydroxide. There was no significant influence of the use of ferrous chloride and lime on routine plant operation throughout the program other than this additional weight and volume of sludge, with a corresponding increase on the load in the digestion process and sludge handling equipment.

Variations in plant load and in the mode of digester operation did not permit a long-term study of sludge handling requirements during this program. The recirculation of suspended solids to the primary settlers from the digester supernatant also interfered with the determination of solids balances, a condition which prevailed at Mentor even prior to the start of ferrous iron and lime addition.

Raw Sludge Production

The quantity of sludge removed at Mentor varied widely from day to day, depending mainly on one or a combination of three factors:

1. Composition of the sludge, including the proportion of chemical additives.
2. Characteristics of the digester supernatant and frequency of return.
3. Hydraulic overloading, with consequent inconsistencies in the quantity of sludge removed during the period of overloading.

Short term tests indicated that in no case was the volume of sludge produced by treatment with ferrous chloride and lime more than double that produced by primary treatment without chemicals. Part of the increase was due to increased solids return from the overloaded digester.

Sludge Digestion

The No. 1 digester was designed for a minimum of 28 days digestion at 98° F. Prior to the iron-lime phosphate removal test period the digester residence time was a minimum of 36 days while during the test period residence time ranged from 8 to 14 days. The decrease in digestion time arose from three major factors:

1. Increase in plant wastewater flow rate from an average of 2.39 MGD in 1968 to 4.36 MGD in 1970.
2. Increased suspended solids removal and the formation of inorganic iron phosphate along with other iron, calcium, and magnesium precipitates from the iron-lime treatment.
3. The creation of a primary settler-digester recycle load of up to 100 percent due to poor No. 2 digester settling. This was caused by the short digestion time and by a low digestion temperature due to heat exchanger overloading.

Although digester residence time was shortened, stabilization did occur and the superior dewatering characteristics of the iron-lime sludge aided in its efficient disposal. Further, a decrease in both total and soluble phosphorus concentrations in the digester supernatant liquor was observed during and immediately following the periods of chemical treatment. The volatile solids of the digested sludge averaged 41.9 percent during a typical test with iron and lime. Some deterioration in sludge digestion was observed during treatment with ferrous chloride and lime when accompanied by low digester temperatures

as determined by a decrease in gas production. Sludge was examined on several occasions and only trace amounts of soluble iron and phosphorus were found, although large amounts of insoluble iron and phosphorus were recirculating in the digester supernatant as shown in Table XIII.

TABLE XIII

Typical Iron and Phosphorus Analyses During Sludge Handling

Note: all quantities expressed in mg/l	<u>Primary Sludge Analysis</u>		Digester Supernatant
	Raw	Digested	
Total Iron	3750.0	1020.0	3950.0
Soluble Iron	105.0	26.0	trace
Total Phosphorus (asP)	1140.0	393.0	1240.0
Soluble Phosphorus	81.5	32.7	6.6

Gas Production

Treatment of sewage with ferrous chloride and lime was not observed to inhibit the bacterial destruction of organic solids by the formation of methane and carbon dioxide in the digesters. However, gas production did decrease as temperature in the heated digester decreased, a condition typically observed with high solids influents, hydraulic overloading and cold weather operation.

Supernatant Return

The return of digester supernatant liquor to the plant process adversely affected the overall removal of phosphorus. The suspended solids in the supernatant return averaged approximately 13,900 pounds per day during a typical test, ranging from approximately 2,200 to 14,800 pounds per day, at concentrations of between 0.5 and 8.5 percent. Less than 15 percent of the returns contained fewer than 1.0 percent solids, and the average was 4.0 percent.

The settling properties of the high solids supernatants were extremely poor, which can be attributed to the reduced residence time and temperature in the heated digester. On many days the sludge that was withdrawn for filtering contained less than five percent more solids than the

supernatant itself. Laboratory cylinder tests indicated no continued settling over a twenty-four hour period. However, adequate settling was observed when the sludge was diluted with an equal volume of water. Additions of polymer were ineffective.

All factors indicated that a simple digester system overload existed that could be corrected by the addition of digester volume and heating capacity.⁹

Sludge Dewatering Tests and Conditioning with Coal

The Mentor Plant disposes of digested sludge solids by conditioning with ferric chloride and lime, filtering on a rotary vacuum filter and land filling of the resultant filter cake. Conditioning of the digested sludge before filtration is accomplished by adding approximately 17 parts of lime and 5 parts of ferric chloride per 100 parts of sludge (all by weight and on a dry basis). The chemicals are mixed with water on a two pounds per gallon basis before adding to the sludge.

Laboratory tests were made to determine the dewatering properties of sludge conditioned with pulverized coal in addition to the ferric chloride and lime. The test method used a 0.1 sq. ft. Buchner funnel in the manner similar to that normally used with a test leaf filter. A vacuum was applied to the Buchner, a coarse filter paper fitted to it, and the funnel was immersed in conditioned sludge. The filtration cycle was one minute with one half the time immersed and the rest drying. The test variables and results are summarized in Table XIV. The results indicated no significant improvement from the use of pulverized coal.

TABLE XIV
Sludge Dewatering Tests:
Use of Coal for Sludge Conditioning¹

Date	Coal	Vacuum Inches of Mercury	Percent Solids	Percent Sludge Solids	Filtrate gal per sq ft per hr	Solids, dry lbs per sq ft per hr
3-13-69	1/2 lb/gal -30+80 mesh	16.0	5.2	23.7	28.6	20.2
3-13-69	--	12.5	5.2	16.8	27.3	13.2
3-14-69	1/2 lb/gal -30+80 mesh	16.0	10.8	22.0	28.6	38.8
3-14-69	--	16.0	10.8	23.0	29.5	40.4
4-03-69	1/2 lb/gal -325 mesh	13.5	8.5	18.5	36.2 (clear)	56.1
4-03-69	--	9.0	8.5	16.8		42.3

¹ All sludge pre-conditioned with ferric chloride and lime.

Section VI

SEWAGE TREATMENT WITH FERROUS IRON AND LIME

This section is a discussion of phosphate precipitation in primary sewage treatment by ferrous iron additions and is based on the experimental results presented in Section V. Emphasis is placed on preferred parameters of operation and suggestions for succeeding applications of the method. Mention of options available with the use of ferrous iron is made where appropriate. The Section concludes with an evaluation of expected treatment costs.

Work at the Mentor Plant demonstrated that additions of ferrous chloride without supplements to an existing primary process were effective in precipitating the contained phosphorus in the raw influent. The precipitation reaction proceeded to rapid completion under turbulent conditions and once the phosphorus was insolubilized, the overall efficiency of removal depended on the particulate material being delivered to the primary settler in a settleable form.

The use of a primary settler to separate the insolubilized precipitate was not effective when ferrous iron was used alone, due to a tendency of the finely-divided precipitates to carry over into the effluent. This is not a process characteristic, but is the direct result of the physical characteristics of primary treatment. With means available in a secondary plant for separation of the iron-phosphate floc from the waste stream, phosphorus removals in excess of 90 percent have been reported.¹⁰ However, the use of a primary system alone, or in combination with supplemental processes where carryover of the floc is undesirable, requires the addition of a base such as lime or caustic soda to attain adequate separation.

The minimum amount of iron additive required is based on the weight of contained iron necessary to react stoichiometrically with the contained phosphate as "P" with no allowance for excess, and is 2.70:1. Plant tests indicate that 3.1 weights of ferrous iron per weight of contained phosphorus, as P, are required for efficient phosphorus precipitation, provided that this is taken as an overall average for a day's operation. A diurnal division of chemical feed was used in this program, with specific quantities needed derived from statistical observation of fluctuations in the influent phosphorus concentrations.

Criteria for Selection of a Base

When a strong base is added to the sewage subsequent to the iron addition, a bulky floc is formed which entrains the iron phosphate precipi-

pitite and flocculates iron present in excess of the stoichiometric minimum, -- the latter appearing as hydroxides. Separation of the phosphate from the sewage is then accomplished by settling of the mixed floc. Control of pH is an important factor. Ferrous iron reacts with phosphates in sewage of neutral pH, but raising the pH to the range of 7.5 to 8.0 insures satisfactory floc formation.

The addition of lime to raw sewage pre-treated with ferrous iron promoted floc formation during the work at Mentor, which aided in settling. The proportion by weight of lime to iron was most influential on effective settling. Plant data indicate that the preferred proportion of lime to iron, by weight, ranges from 1.6:1 to 1.9:1, the precise proportion requiring experimental adjustment in each plant application.

There is limited evidence that contribution of calcium ions by the lime results in the formation of a certain amount of calcium phosphate even at relatively low pH levels; but calcium precipitation is not considered to present a particular cost advantage in this case.

Data from actual plant testing therefore indicate that with a 3.1:1 weight ratio of Fe:P and a weight ratio of lime to iron varying from 1.6:1 to 1.9:1, phosphorus removals of approximately 80 percent can be attained. A lime-to-iron weight ratio of 1.9:1 is recommended in future applications with the expectation that refinements in procedure and dosing equipment will permit reductions in the required quantities. With filtration or bioflocculation of the residual iron-phosphate precipitate in the effluent, removals in excess of 90 percent may be expected.

The addition of additives supplemental to ferrous chloride and lime is recommended for further study. When considered in terms of overall performance, the degree of treatment attained with their use was not significantly different from that obtained with ferrous chloride and lime alone. The principal advantage of using coagulants would be to accomplish enhanced suspended solids removal. However, at the Mentor Plant there was no provable need for their routine use. A precise determination of the advantages obtained from coal use could not be determined. The use of supplements might be valuable should ferrous chloride and lime be used in a plant other than at Mentor. An evaluation of these materials, with particular emphasis on cost comparison, could be of advantage; however, optimization of ferrous chloride and lime additions should be undertaken at the same time to insure a base line of control.

Chemical Costs

The cost of phosphorus removal by the addition of ferrous iron pickle liquor and lime is reflected mainly in the two categories of chemicals and equipment. The labor required is minimal, and consists mainly of monitoring, unloading and storage of chemicals, and the filling of feeders. On the basis of plant experience these activities can be accommodated by the normal plant staff, and provision for labor specific to the phosphorus removal operation is therefore not included as a general requirement.

Chemical Sources

Ferrous iron reacts with dissolved orthophosphates and is the cheapest of the known chemical precipitants. A common commercial form is the hydrated salt, produced as a low cost source of iron in fertilizers. However, ferrous iron--either as the chloride or sulfate--is also available as spent pickling acid, "pickle liquor", from the acid cleaning of steel.

Laboratory work prior to plant testing at Mentor demonstrated the equal effectiveness of both common ferrous forms--chloride and sulfate--and both are recommended for use as local supplies permit. The specifications for ferrous chloride pickle liquor used at Mentor were generally satisfied by the supplier; however, occasional delivery of materials high in trace elements, or low in iron content; did occur. No deleterious effects on treatment were noted by such deviations, suggesting that wider latitude can be employed in future applications. Testing of random samples of waste pickle liquor is therefore suggested to determine on a plant scale whether restrictive specifications will be required in future applications. It should be understood that pickle liquor or other additives must contain no impurities which would cause the effluent to present any hazard or to interfere with subsequent use of the discharged water.

At present ferrous iron pickle liquor is available at no cost except that of freight and possibly nominal handling charges. The delivered cost of iron as pickle liquor, based on truck haulage of thirty miles, has been quoted at \$0.02 per pound of contained iron. This price is assumed in the estimation of operating costs. The delivered cost of hydrated lime, in bags, ranges typically between \$20.00 and \$23.00 per ton. The latter value is used in this estimate.

Equipment Costs

Actual equipment cost will vary in every case according to both the plant capacity and the phosphorus concentration of the wastewater, and

must therefore be discussed here only in general terms. Installation of certain equipment and facilities discussed here but not used during the experimental program may be expected to increase substantially the effectiveness of ferrous chloride and lime additions.

Equipment requirements may be divided into two groups: Items required as a minimum in any plant for the handling and feeding of chemicals, and items which may or may not be required for the handling of sludge.

Chemical Feed Equipment

Pickle liquor is received as an acidic solution containing 5 to 10 percent by weight of iron; and a suitable non-corroding storage reservoir is required. For optimum phosphorus removal and economy the pickle liquor is metered into the raw sewage on a continuous basis by a variable-rate positive displacement pump with the rate varied in proportion to the total amount of phosphorus contained in the influent.

As in all methods of chemical phosphate removal, the rate of chemical feed should be proportioned to the concentration of influent phosphorus. Where the daily fluctuations in phosphorus content are reasonably well known and predictable the pump may be adjusted manually, though this method usually results in the addition of either an excess or deficiency of chemical at any given time. A desirable alternative is the installation of an automatic phosphorus analyzer, with iron feed control continuously adjusted on the basis of the running analysis. Several experimental analyzers are available with roughly comparable performance, at prices ranging between twenty and thirty thousand dollars.

As in the case of any chemical reaction, effective mixing is required and a zone of turbulence is recommended for effective mixing of ferrous iron solution with sewage. Approximately 40 gallons of 7 percent pickle liquor are required per million gallons of sewage for each mg/l of contained phosphorus, and optimum results are obtained only when the liquid is well mixed into the sewage. On the basis of this plant study special mixing equipment is not needed when the pickle liquor can be introduced into a region of turbulence, such as at a pump station. Air was used in this program for additional mixing due to the hydraulic overloading at the Mentor Plant and subsequently shortened primary detention times. In special cases flash mixing might be necessary.

Lime must also be metered into the sewage, in proportion to the rate of iron addition. The feeder may be adjusted manually, subject to the

same conditons that apply to iron; but when automatic analysis and proportioning control are available, the lime feeder can be controlled by the same signal that controls the iron feeder plus adjustments to attain a suitable pH.

Lime may be introduced in the dry form, but is not efficiently mixed except in a zone of extreme turbulence. Continuous conversion of the dry lime to a water slurry after metering is recommended, with the slurry then mixed into the sewage as in the manner of the pickle liquor.

All of the chemical handling equipment can be added to an existing primary treatment plant and used, or not used, as desired without interference with the basic plant structure or operation. In the event the plant is later expanded to secondary activated sludge treatment, where lime is not required as a supplement to the iron, the installation can be used directly with only the retirement of the lime handling facility.

Treatment Cost

At the recommended dosage of 3.1 weights of iron per weight of contained phosphorus, as P, a total of 25.9 pounds of iron is required per million gallons for each mg/l of contained phosphorus, representing an iron cost of \$0.52.

At the recommended maximum dosage of 1.9 weights of hydrated lime per weight of iron, equivalent to 5.9 weights of lime per weight of phosphorus, 49.2 pounds of lime are required per million gallons for each mg/l of phosphorus, representing a lime cost of \$0.57.

The combined chemical cost, then, is \$1.09 per million gallons of sewage treated, for each mg/l of contained phosphorus. Total chemical cost is this value times the phosphorus concentration of the influent wastewater in milligrams per liter. For example, in the case of a sewage containing 13 mg/l phosphorus, as was typically received at the Mentor Plant, the total chemical cost would be \$14.17 per million gallons.

Sludge Handling

The weight and volume of sludge produced in a conventional primary plant--and thus the size and actual cost of digesters or other sewage handling equipment--vary in each case with the plant flow and with the concentration and nature of the solids removed from the sewage. The requirement for special sludge handling conditions, if necessary at

all, therefore can be measured only for each plant situation.

The weight increase in sludge solids due to the precipitation of phosphates by ferrous iron and lime was difficult to determine at the Mentor Plant by direct observation due to the digester overload conditions which existed. The use of the chemicals increased the suspended solids removals from an average of 35.8 percent when no chemicals were used to an average of 61.5 percent. At an average of 190 mg/l suspended solids content in the raw sewage this is an increase of approximately 420 pounds to a total of approximately 975 pounds removed per million gallons of raw sewage.

The use of ferrous chloride and lime will produce approximately 100 pounds of various iron and calcium phosphate, hydroxide, carbonate, etc., compounds per mg/l of phosphorus contained in the raw sewage. At approximately 13 mg/l of phosphorus in the raw sewage, this represents 1300 pounds of additional sludge per million gallons. The expected total sludge solids produced was approximately 2300 pounds. For an extended period, an average of 6134 pounds per million gallons were pumped to the digesters with more than one half of that contributed by the supernatant return.

The important factor of sludge volume increase is also variable according to influent sewage composition and plant efficiency, but in no case appears to be more than twice that obtained in normal primary treatment.

Waste sludge from ferrous chloride and lime treatment was thickened and disposed of by the techniques normally employed at the Mentor Plant. The increased volumes of sludge caused digester temperature to drop and solids concentration in the digester supernatant to increase to very high levels. The phosphorus contained in the sludge remained insoluble throughout sludge treatment and was not resolubilized in the digester supernatant.

The determination of sludge handling cost for iron-lime treatment must be made for each plant. As a maximum the cost difference will be that of doubling the capacity of the facility. As a minimum no increase is necessary. In the Mentor Plant, the capacity of the digesters and filters was taxed, to be sure, but not to the point of breakdown. An increased capacity would have resulted in a greater improvement in degree of treatment due to the recirculation of fewer solids in the digester supernatant, but was not mandated by the use of ferrous iron.

Section VII

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TABLE XV
Summary of Experimental Conditions

Test Chemical Additions No. by Type and Combination	No. Days In Test	Flow Rate mgd	Influent Acidity as CaCO ₃ mg/Liter	Chemical Additions mg/Liter			Application of Air for Mixing cu. ft./min.
				Fe	Lime	Other	
1) None	9	3.210	-	-	-	-	85.0 West Tank
2) None	7	2.670	-	-	-	-	85.0 East Tank
3) Ferrous Chloride ¹ , FeCl ₂	4	2.674	-	41.0	-	-	85.0 East Tank
4) Ferrous Chloride, FeCl ₂	7	3.830	-	49.0	-	-	85.0 West Tank
5) Hydrated Lime, Ca(OH) ₂	5	2.205	-	-	69.6	-	85.0 East Tank
6) Hydrated Lime, Ca(OH) ₂	7	2.630	-	-	63.0	-	85.0 West Tank
7) Ferrous Chloride & Lime	13	3.678	-	43.0	55.0	-	85.0 East Tank
8) Ferrous Chloride & Lime	11	2.710	-	50.0	103.0	-	85.0 East Tank
9) Ferrous Chloride & Lime	11	3.680	-	49.0	78.0	-	42.5 Each Tank
10) Ferrous Chloride & Lime	40	3.970	-	38.8	75.0	-	42.5 Each Tank
11) Ferrous Chloride & Lime	9	4.250	48	42.2	68.7	-	42.5 Each Tank
12) Ferrous Chloride & Lime	13	4.210	26	39.6	82.0	-	42.5 Each Tank
13) Ferrous Chloride & Lime	17	4.500	21	33.7	68.3	-	42.5 Each Tank
14) Polyelectrolyte, Dow A-23 ²	31	3.510	-	-	-	0.65	No Atr
15) Polyelectrolyte, Dow A-23	7	2.520	-	-	-	0.42	85.0 East Tank
16) Polyelectrolyte, Dow A-23	5	2.338	-	-	-	0.45	85.0 West Tank
17) Ferrous Chloride & Dow A-23	11	4.610	-	48.0	-	0.43	85.0 East Tank
18) Lime & Dow A-23	2	2.545	-	-	88.0	0.47	42.5 Each Tank
19) Ferrous Chloride, Lime & Calgon 3000	19	3.000	46	47.0	101.0	0.26	42.5 Each Tank
20) Ferrous Chloride, Lime & Diamond 630	11	4.752	21	35.7	75.6	0.26	42.5 Each Tank
21) Ferrous Chloride, Lime & Diamond 640	10	4.050	21	43.0	82.0	0.25	42.5 Each Tank
22) Ferrous Chloride, Lime & Dow A-23	89	4.460	45	46.0	83.0	0.45	42.5 Each Tank
23) Ferrous Chloride, Lime & Sodium Silicate ³	17	4.030	30	46.0	87.0	12.0 ³	42.5 Each Tank
24) Ferrous Chloride, Lime & Coal ⁴	22	3.800	-	48.0	67.0 ²	30.0 ⁴	42.5 Each Tank
25) Dow A-23 & Coal ⁵	5	3.033	-	Poly→	0.74 ²	51.6 ⁵	42.5 Each Tank

¹ Pickle liquor; 7-10% Fe by weight

² Dow A-23 polyelectrolyte; 0.3% solution

³ Grade 40 silicate; 40% Na₂SiO₃

⁴ 18 x 80 mesh coal; added to east primary only

⁵ Minus 80 mesh coal; added to east primary only

TABLE XVI
Summary of Experimental Results: Solids Removal

Test Chemical Additions No. by Type and Combination	No. Days In Test	Flow Rate mgd	Chemical Additions mg/Liter			Total Solids mg/Liter		Suspended Solids mg/Liter		
			Fe	Lime	Other	IN	OUT	IN	OUT	%Red
1) None	9	3.210	-	-	-	845	705	132	91	31.0
2) None	7	2.670	-	-	-	840	766	198	118	40.5
3) Ferrous Chloride, ¹ FeCl ₂	4	2.674	41.0	-	-	834	755	226	164	28.5
4) Ferrous Chloride, FeCl ₂	7	3.830	49.0	-	-	805	797	193	166	14.0
5) Hydrated Lime, Ca(OH) ₂	5	2.205	-	69.6	-	752	690	254	99	61.0
6) Hydrated Lime, Ca(OH) ₂	7	2.630	-	63.0	-	752	702	188	88	53.3
7) Ferrous Chloride & Lime	13	3.678	43.0	55.0	-	730	719	119	64	46.2
8) Ferrous Chloride & Lime	11	2.710	50.0	103.0	-	651	690	138	67	51.5
9) Ferrous Chloride & Lime	11	3.680	49.0	78.0	-	753	774	164	43	73.8
10) Ferrous Chloride & Lime	40	3.970	38.8	75.0	-	785	779	181	87	52.0
11) Ferrous Chloride & Lime	9	4.250	42.2	68.7	-	748	739	187	77	58.8
12) Ferrous Chloride & Lime	13	4.210	39.6	82.0	-	757	773	193	62	67.9
13) Ferrous Chloride & Lime	17	4.500	33.7	68.3	-	755	731	178	62	65.2
14) Polyelectrolyte, Dow A-23 ²	31	3.510	-	-	0.65	925	700	198	87	56.1
15) Polyelectrolyte, Dow A-23	7	2.520	-	-	0.42	810	742	233	139	40.4
16) Polyelectrolyte, Dow A-23	5	2.338	-	-	0.45	844	719	187	100	46.5
17) Ferrous Chloride & Dow A-23	11	4.610	48.0	-	0.43	778	792	152	144	5.2
18) Lime & Dow A-23	2	2.545	-	88.0	0.47	752	753	171	106	38.0
19) Ferrous Chloride, Lime & Calgon 3000	19	3.000	47.0	101.0	0.26	710	721	146	43	70.6
20) Ferrous Chloride, Lime & Diamond 630	11	4.752	35.7	75.6	0.26	755	702	174	62	64.4
21) Ferrous Chloride, Lime & Diamond 640	10	4.050	43.0	82.0	0.25	752	743	171	49	71.4
22) Ferrous Chloride, Lime & Dow A-23	89	4.460	46.0	83.0	0.45	758	782	183	69	62.3
23) Ferrous Chloride, Lime & Sodium Silicate ³	17	4.030	46.0	87.0	12.0 ³	640	762	216	63	70.9
24) Ferrous Chloride, Lime & Coal ⁴	22	3.800	48.0	67.0	30.0 ⁴	720	722	157	64	59.3
25) Dow A-23 & Coal ⁵	5	3.033	Poly-0.74 ²		51.6 ⁵	790	739	167	93	44.4

¹ Pickle liquor; 7-10% Fe by weight

² Dow A-23 polyelectrolyte; 0.3% solution

³ Grade 40 silicate; 40% Na₂SiO₃

⁴ 18 x 80 mesh coal; added to east primary only

⁵ Minus 80 mesh coal; added to east primary only

TABLE XVII
Summary of Experimental Results: Oxygen Demand Reduction

Test Chemical Additions No. by Type and Combination	No. Days In Test	Flow Rate mgd	Chemical Additions mg/Liter			BOD mg/Liter			COD mg/Liter		
			Fe	Lime	Other	IN	OUT	%Red	IN	OUT	%Red
1) None	9	3.210	-	-	-	153	123	19.5	232	182	21.4
2) None	7	2.670	-	-	-	192	194	-	251	203	19.1
3) Ferrous Chloride ¹ , FeCl ₂	4	2.674	41.0	-	-	187	134	28.3	505	339	32.8
4) Ferrous Chloride, FeCl ₂	7	3.830	49.0	-	-	155	113	27.0	385	328	14.7
5) Hydrated Lime, Ca(OH) ₂	5	2.205	-	69.6	-	143	119	16.7	482	350	27.4
6) Hydrated Lime, Ca(OH) ₂	7	2.630	-	63.0	-	224	185	17.3	450	293	34.8
7) Ferrous Chloride & Lime	13	3.678	43.0	55.0	-	161	72	55.3	380	148	61.1
8) Ferrous Chloride & Lime	11	2.710	50.0	103.0	-	135	86	36.4	320	166	48.2
9) Ferrous Chloride & Lime	11	3.680	49.0	78.0	-	174	71	59.2	542	262	51.7
10) Ferrous Chloride & Lime	40	3.970	38.8	75.0	-	198	73	63.2	410	179	56.3
11) Ferrous Chloride & Lime	9	4.250	42.2	68.7	-	205	78	61.9	515	163	68.4
12) Ferrous Chloride & Lime	13	4.210	39.6	82.0	-	201	74	63.2	433	190	56.2
13) Ferrous Chloride & Lime	17	4.500	33.7	68.3	-	192	85	55.7	395	202	47.8
14) Polyelectrolyte, Dow A-23 ²	31	3.510	-	-	0.65	173	123	28.8	263	177	32.7
15) Polyelectrolyte, Dow A-23	7	2.520	-	-	0.42	188	144	23.3	326	171	47.6
16) Polyelectrolyte, Dow A-23	5	2.338	-	-	0.45	173	145	16.2	319	228	28.6
17) Ferrous Chloride & Dow A-23	11	4.610	48.0	-	0.43	192	139	27.6	352	244	30.7
18) Lime & Dow A-23	2	2.545	-	88.0	0.47	173	133	23.1	260	175	32.6
19) Ferrous Chloride, Lime & Calgon 3000	19	3.000	47.0	101.0	0.26	151	73	51.7	460	163	64.6
20) Ferrous Chloride, Lime & Diamond 630	11	4.752	35.7	75.6	0.26	173	84	51.4	445	221	50.3
21) Ferrous Chloride, Lime & Diamond 640	10	4.050	43.0	82.0	0.25	222	80	64.0	412	206	50.0
22) Ferrous Chloride, Lime & Dow A-23	89	4.460	46.0	83.0	0.45	136	98	27.9	405	158	61.0
23) Ferrous Chloride, Lime & Sodium Silicate ³	17	4.030	46.0	87.0	12.0 ³	239	80	66.5	490	231	52.8
24) Ferrous Chloride, Lime & Coal ⁴	22	3.800	48.0	67.0	30.0 ⁴	180	97	46.2	505	247	51.1
25) Dow A-23 & Coal ⁵	5	3.033	Poly	0.74 ²	51.6 ⁵	184	112	39.1	468	273	63.1

¹ Pickle liquor; 7-10% Fe by weight

² Dow A-23 polyelectrolyte; 0.3% solution

³ Grade 40 silicate; 40% Na₂SiO₃

⁴ 18 x 80 mesh coal; added to east primary only

⁵ Minus 80 mesh coal; added to east primary only

TABLE XVIII
Summary of Experimental Results: Phosphorus Removal

Test Chemical Additions No. by Type and Combination	No. Days	Flow Rate In mgd	Chemical Additions mg/Liter			Total Phosphorus (as P) mg/Liter			pH		Effluent Iron mg/Liter	
			Fe	Lime	Other	IN	OUT	%Red	IN	OUT	IN	OUT
1) None	9	3.210	-	-	-	15.5	16.4	-	7.5	7.5	-	-
2) None	7	2.670	-	-	-	14.0	16.2	-	7.8	7.6	-	-
3) Ferrous Chloride, FeCl_2 ¹	4	2.674	41.0	-	-	16.7	12.8	23.4	7.7	7.3	-	-
4) Ferrous Chloride, FeCl_2	7	3.830	49.0	-	-	14.2	10.5	26.0	7.5	7.0	42.5	-
5) Hydrated Lime, Ca(OH)_2	5	2.205	-	69.6	-	16.3	9.5	41.8	7.4	8.5	-	-
6) Hydrated Lime, Ca(OH)_2	7	2.630	-	63.0	-	14.8	8.2	44.7	7.7	8.6	-	-
7) Ferrous Chloride & Lime	13	3.678	43.0	55.0	-	12.1	3.7	69.4	7.1	6.9	16.9	-
8) Ferrous Chloride & Lime	11	2.710	50.0	103.0	-	10.5	4.2	60.0	7.7	7.4	9.9	-
9) Ferrous Chloride & Lime	11	3.680	49.0	78.0	-	14.1	2.6	81.6	7.3	7.6	8.7	-
10) Ferrous Chloride & Lime	40	3.970	38.8	75.0	-	12.3	3.1	74.8	7.6	7.6	13.2	-
11) Ferrous Chloride & Lime	9	4.250	42.2	68.7	-	13.7	2.3	83.2	7.5	7.7	10.8	-
12) Ferrous Chloride & Lime	13	4.210	39.6	82.0	-	12.9	2.4	81.4	6.9	7.9	11.0	-
13) Ferrous Chloride & Lime	17	4.500	33.7	68.3	-	12.9	2.6	79.8	7.4	7.2	10.6	-
14) Polyelectrolyte, Dow A-23 ²	31	3.510	-	-	0.65	13.1	13.1	0.0	7.7	7.5	-	-
15) Polyelectrolyte, Dow A-23	7	2.520	-	-	0.42	17.8	15.5	12.9	7.6	7.5	-	-
16) Polyelectrolyte, Dow A-23	5	2.338	-	-	0.45	17.6	13.3	24.5	7.5	7.5	-	-
17) Ferrous Chloride & Dow A-23	11	4.610	48.0	-	0.43	12.4	7.2	42.0	7.4	6.9	36.0	-
18) Lime & Dow A-23	2	2.545	-	88.0	0.47	19.0	10.0	47.4	7.3	9.1	-	-
19) Ferrous Chloride, Lime & Calgon 3000	19	3.000	47.0	101.0	0.26	13.7	2.0	85.4	7.6	8.1	8.3	-
20) Ferrous Chloride, Lime & Diamond 630	11	4.752	35.7	75.6	0.26	10.7	2.1	80.4	7.6	8.0	9.9	-
21) Ferrous Chloride, Lime & Diamond 640	10	4.050	43.0	82.0	0.25	11.9	2.2	81.5	7.2	7.5	10.4	-
22) Ferrous Chloride, Lime & Dow A-23	89	4.460	46.0	83.0	0.45	13.1	2.3	82.5	7.4	7.6	12.8	-
23) Ferrous Chloride, Lime & Sodium Silicate ³	17	4.030	46.0	87.0	12.0 ³	13.1	2.5	80.9	7.3	7.5	13.1	-
24) Ferrous Chloride, Lime & Coal ⁴	22	3.800	48.0	67.0	30.0 ⁴	14.1	2.5	82.3	7.5	7.5	15.8	-
25) Dow A-23 & Coal ⁵	5	3.033	Poly-0.74 ²	51.6 ⁵	13.3	12.2	8.3	7.7	7.1	4.5	-	-

¹ Pickle liquor; 7-10% Fe by weight

² Dow A-23 polyelectrolyte; 0.3% solution

³ Grade 40 silicate; 40% Na_2SiO_3

⁴ 18 x 80 mesh coal; added to east primary only

⁵ Minus 80 mesh coal; added to east primary only

1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
	W		05D	
5	Organization County of Lake, Ohio Court House Painesville, Ohio 44077			
6	Title Phosphorus Removal by Ferrous Iron and Lime			
10	Author(s) Alvord, E. Thomas Gaughan, Dennis M. Marr, Clyde M. Colpetzer, Thomas Rose, Dudley B.		16	Project Designation EPA Project #11010 EGO
			21	Note
22	Citation			
23	Descriptors (Starred First) *Phosphorus Removal, *Waste Treatment, *Pickle Liquor, *Chemical Precipitation, Ferrous Chloride, Iron, Lime Addition, Lake County Ohio			
25	Identifiers (Starred First)			
27	Abstract When used in primary treatment, ferrous iron was effective in removing more than 80 percent of the phosphorus contained in sewage, with spent pickle liquor a satisfactory source of the metal ion. Required iron dosages ranged from the theoretical minimum of 2.7 to a maximum of approximately 3.1 weights of ferrous iron per weight of phosphorus contained in the sewage. When advanced means, such as filtration, are available for more complete removal of the insolubilized phosphate precipitate, phosphorus removals in excess of 90 percent are indicated. Overall suspended solids removals of 61.5 percent were attained over a 23-month plant experimental program, with BOD and COD removals of 61.6 and 55.3 percent, respectively. The combined chemical cost for ferrous chloride pickle liquor and lime was \$1.09 per million gallons of sewage treated, for each mg/l of contained phosphorus. The total chemical costs for treating a sewage containing 13 mg/l of phosphorus as typically received during this work, would be \$14.17 per million gallons.			
Abstractor		Institution		
Patrick M. Tobin		Environmental Protection Agency		